

LA-UR-16-23374

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Title: Seaborg Memorial Lecture: Plutonium Science for the 21st Century

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Intended for: Pu75. Celebration of the Platinum Year of the Discovery of Plutonium,
2016-05-23/2016-05-25 (kalpakkam, India)

Issued: 2016-05-12

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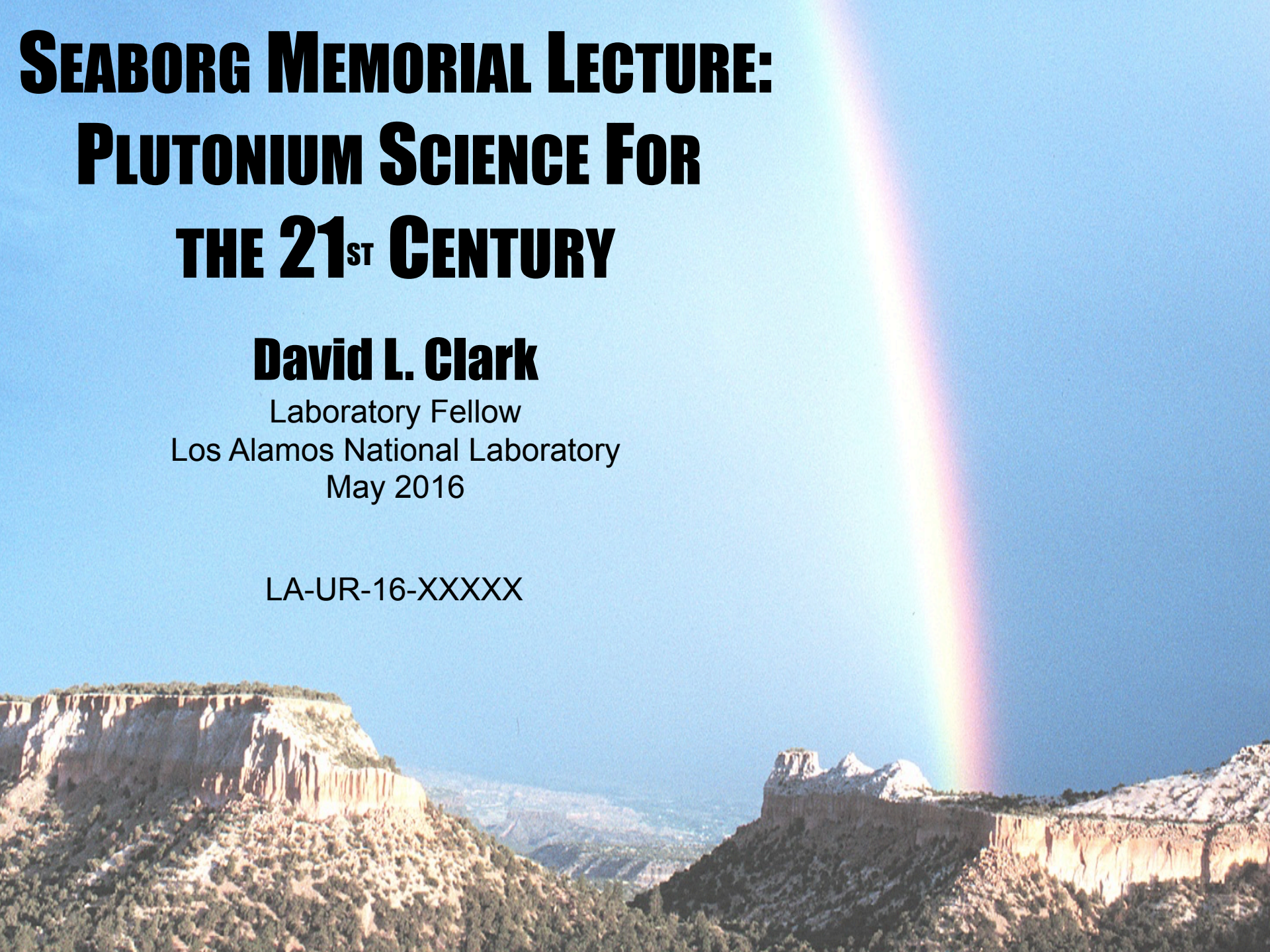
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SEABORG MEMORIAL LECTURE: PLUTONIUM SCIENCE FOR THE 21ST CENTURY

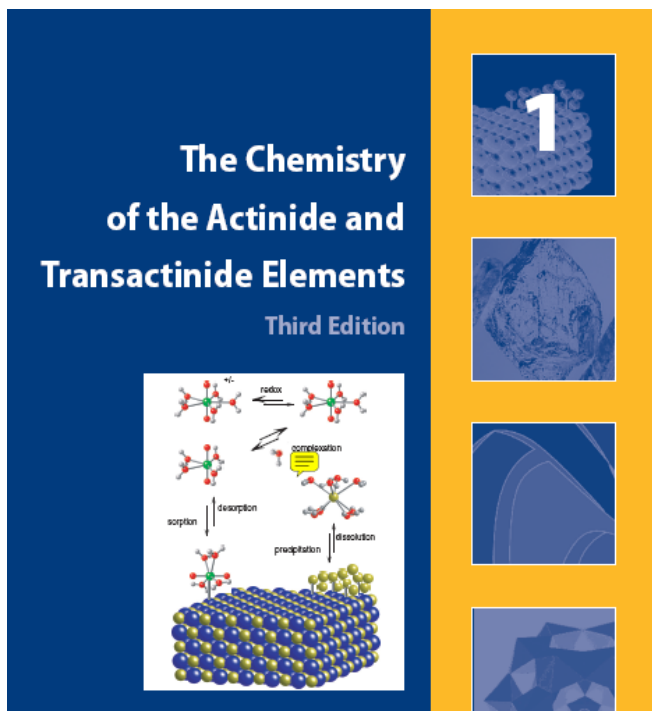
David L. Clark

Laboratory Fellow
Los Alamos National Laboratory
May 2016

LA-UR-16-XXXXX



Source Material



Clark, Hecker, Jarvinen, Neu, *The Chemistry of the Actinide and Transactinide Elements*, Chapter 7, Plutonium, **2006, 813-1264**

Wick, *The Plutonium Handbook*, American Nuclear Society, **1967, 1980**

Challenges in Plutonium Science
Los Alamos Science Number 26, **2000**

Hoffman, *Advances in Plutonium Chemistry 1967-2000*, **2002**

Nitsche, *Chemical Reviews*, **2013, 113**



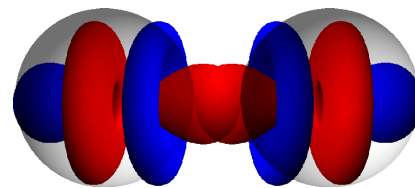
Actinide Elements and the Periodic Table

																		2	He																
1	H																	5	B	6	C	7	N	8	O	9	F	10	Ne						
3	Li	4	Be																	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar				
11	Na	12	Mg																	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr				
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
55	Cs	56	Ba	57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu	118	
87	Fr	88	Ra	89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr		
																				114	Fl			116	Lv										

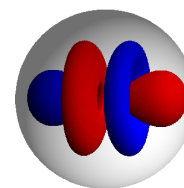
Actinide Elements and 5f Shell Collapse

Metallic state

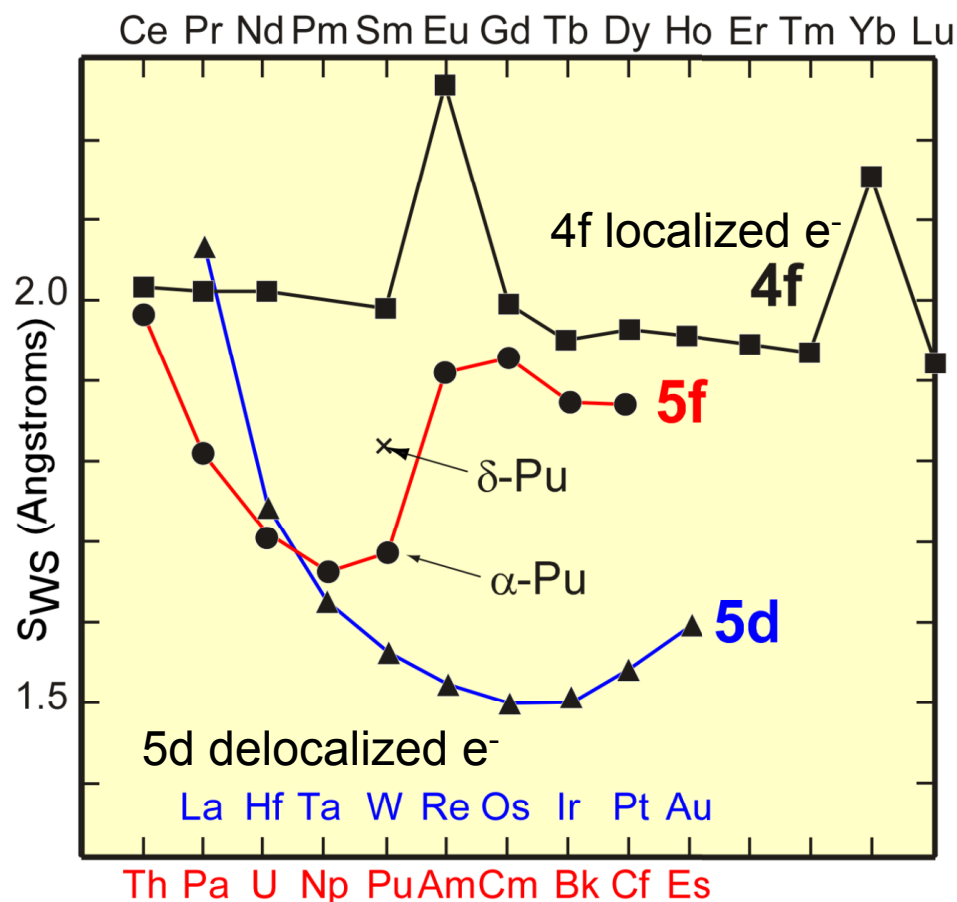
- Outer **7s** and **6d** electrons overlap strongly & have metallic behavior
- Light actinides have metallic-like **5f** electrons
- Heavy actinides have atomic-like **5f** electrons
- The transition from delocalized to localized **5f** electrons (Mott-like) takes place at Pu
- δ -Pu appears to undergo an intermediate transition that is only partly localized!
- Discussion surrounding localized or delocalized **5f** e^- pervades molecular bonding descriptions



Metallic electrons



Atomic electrons



R. Denning, *Struct. Bonding*, 1992, 79, 215
 Savrasov, Kotliar, Abrahams, *Nature*, 2001, 410, 759
 Wills, Eriksson, 2000, *Los Alamos Science*, 26, 128
 R. C. Albers, *Nature*, 2001, 410, 759

How much plutonium is there?

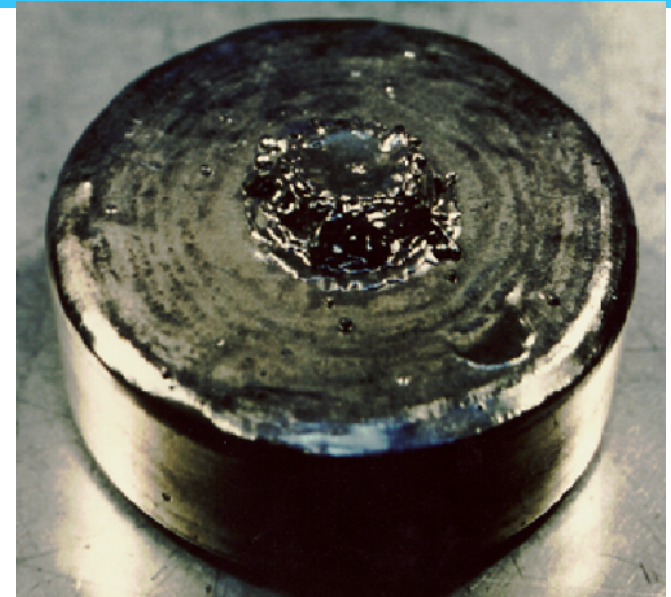
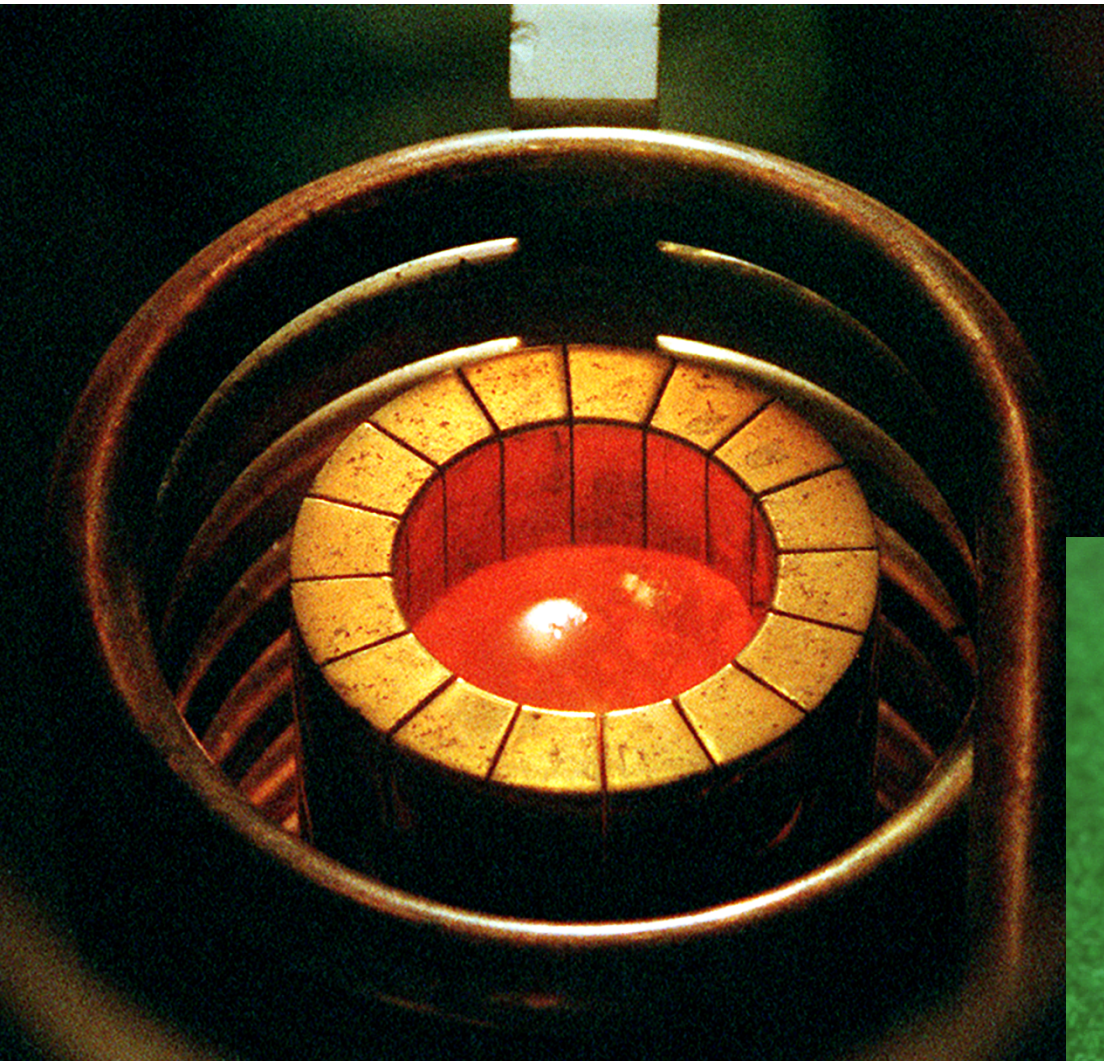
- 2016 Inventory
 - > 2700 metric tons (tonnes)
 - Spent fuel
 - Nuclear weapon's components
 - Various nuclear inventories
 - Legacy materials
 - Wastes
- 495 tons separated Pu
- Complex blend of political, socioeconomic and technological challenges to manage these inventories efficiently and safely

Abright, Kramer, Plutonium Watch, *ISIS*, 2005
Global Fissile Material Report 2014

ISIS = Institute for Science and International Security



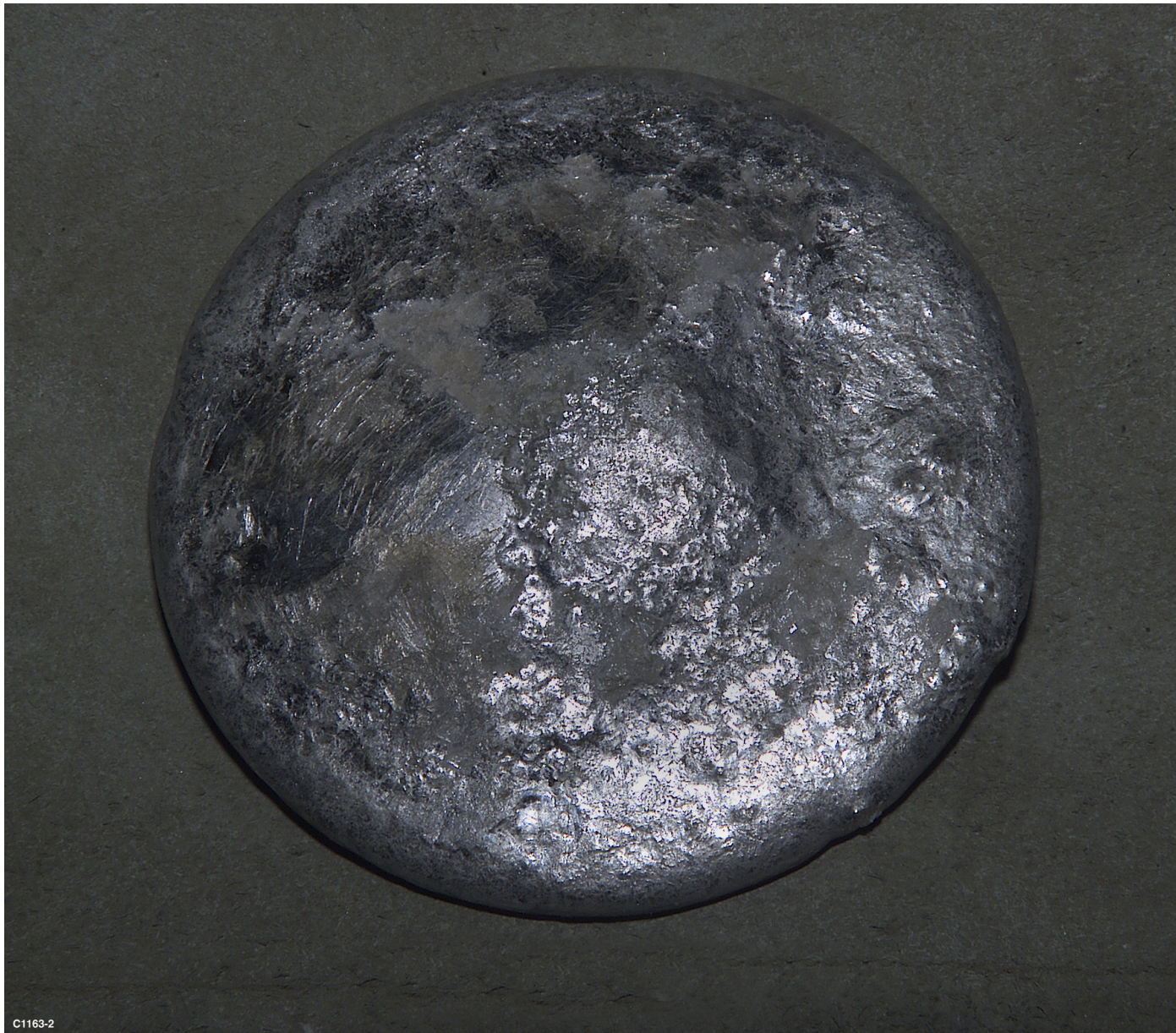
The element plutonium



Jason Lashley *J. Nuclear Materials* 1999, 274, 315

Ingots of ^{239}Pu Metal

7

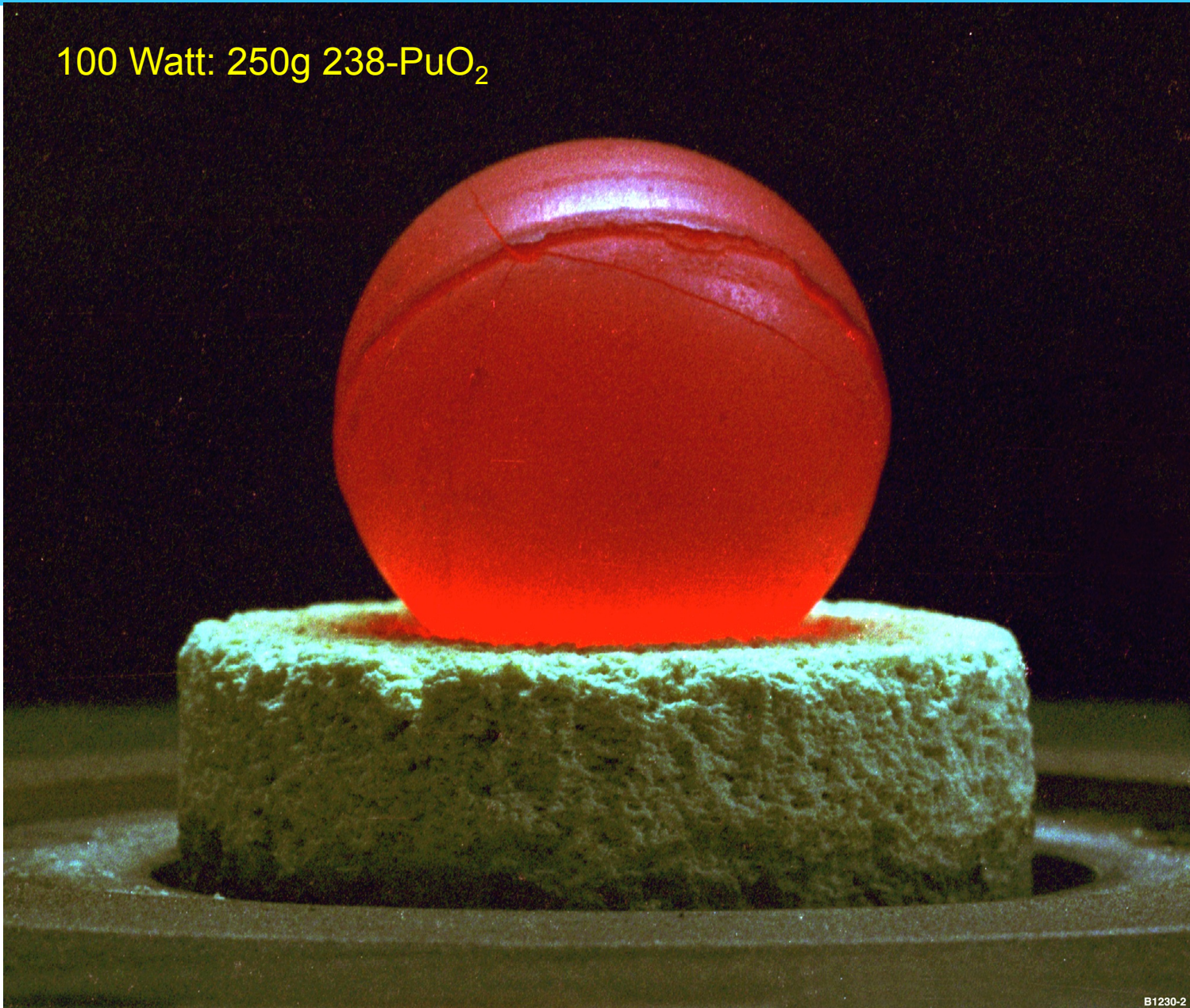


C1163-2

^{238}Pu Oxide Power Source

8

100 Watt: 250g $^{238}\text{PuO}_2$



Higher Oxides: PuO_{2+x}

- Widely held that oxidation of PuO_2 was not possible Clark, et al *Chem Act Transact Elements*, 2006, 813
- PVT, TGA microbalance, MS, and XRD suggested formation of a higher oxide

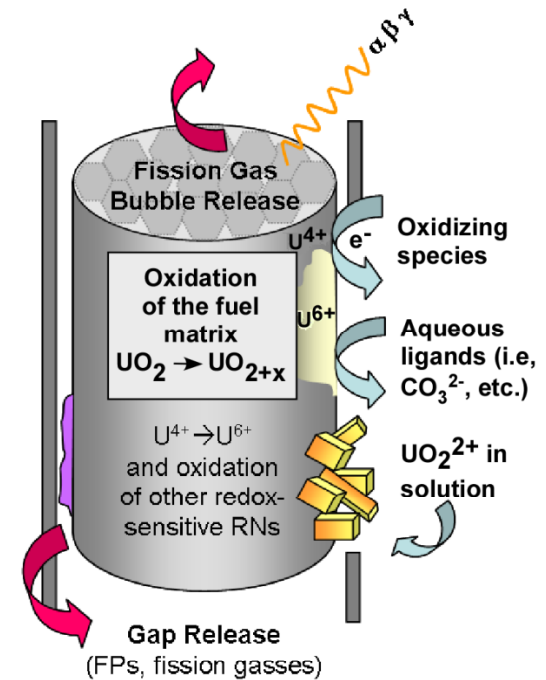


Haschke, Allen, Morales, *Science*, 2000, 287, 285

- Highly controversial for plutonium - challenges established dogma
- However: oxidation of UO_2 to UO_{2+x} is well-known - invoked in spent fuel dissolution

Bruno, Ewing, *Elements*, 2006, 2, 343.

- The PuO_2 - H_2O corrosion reaction generated intense interest & concern
- Pu repackaged in Over 4500 “3013” containers, >13 tonnes – to SRS



Why do we care?

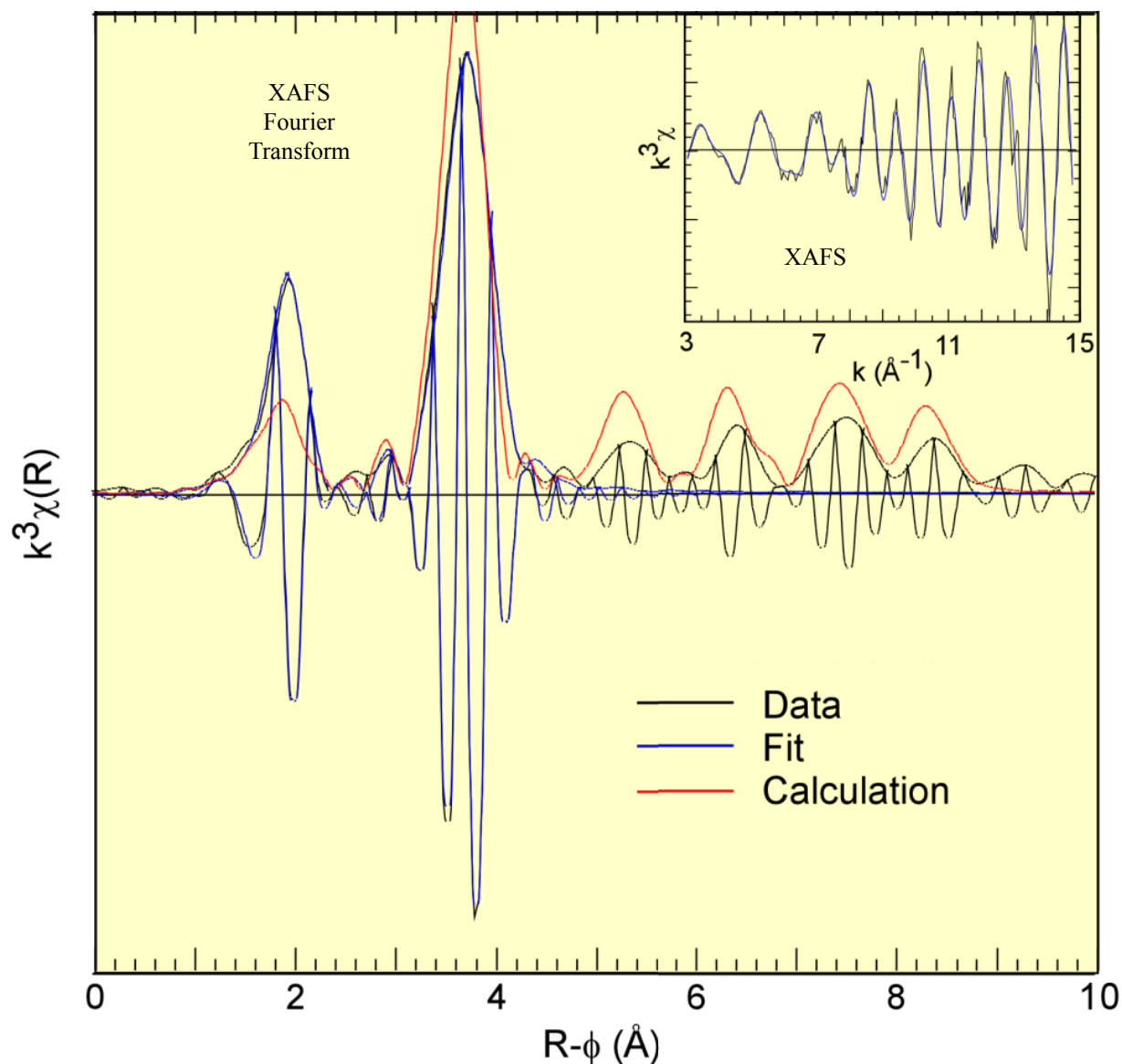
For long-term storage, reactions of H_2O & other gases is of major concern

- Pu materials must be stabilized for 50 years in welded, sealed containers.
- small molecule reactions have led to stoichiometry changes, containment breaches and dispersal of material
- Container pressurization and corrosion are a safety concern



Local Structure of ordered PuO_2 by L_3 -edge XAFS

11

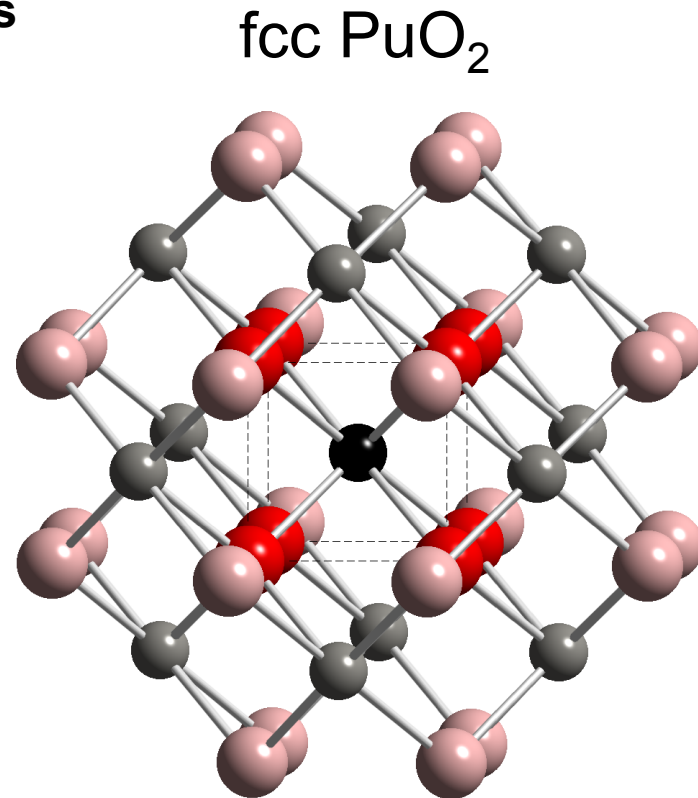
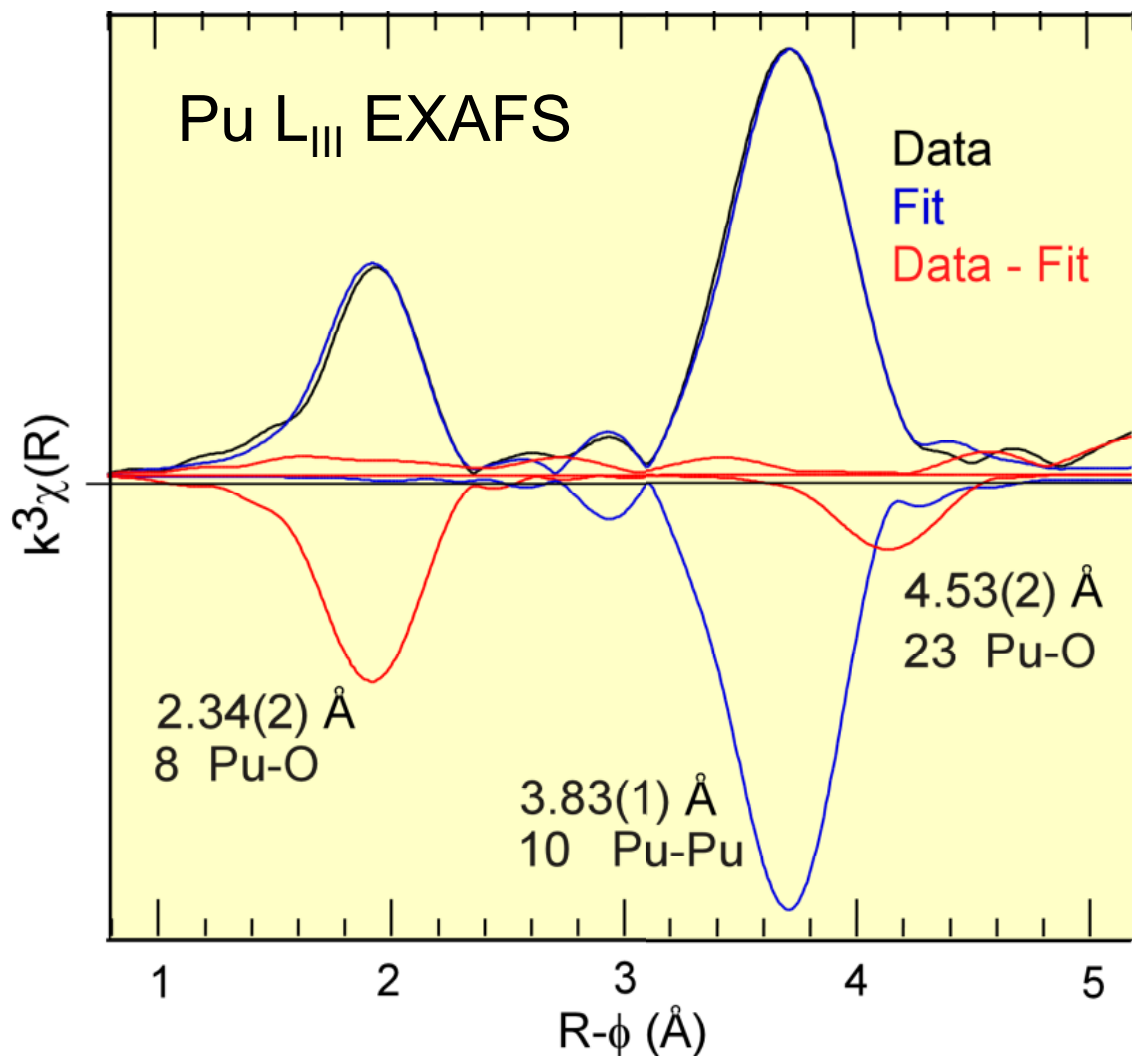


Key Features

- Stoichiometric PuO_2 by rigorous anhydrous preparation
- High degree of ordering out to $R = 8 \text{ \AA}$
- Close correspondence between local and crystallographic structure (FEFF)
 - Including nodes in real part of data
- Differences between data and calculation due to differences in Debye-Waller factors

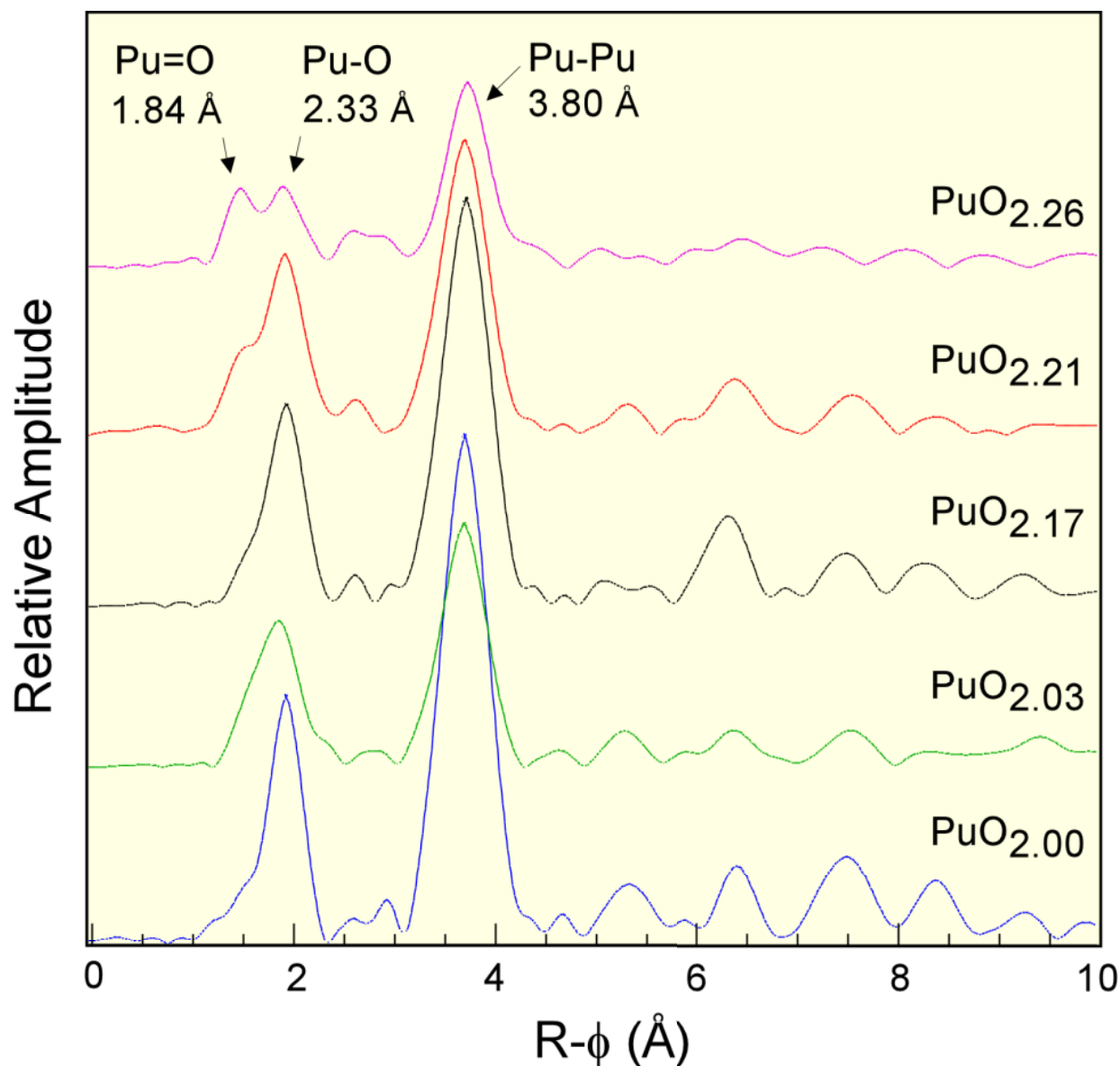
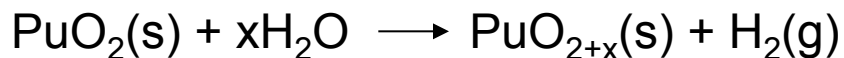
Chemical Speciation from EXAFS

EXAFS data and 3-shell fit of fcc PuO_2 agrees with crystallographic structure



$a_0 = 5.396$ Å
 8 O: 2.33 Å
 12 Pu: 3.81 Å
 24 O: 4.47 Å
 24 Pu: 5.87 Å
 etc.

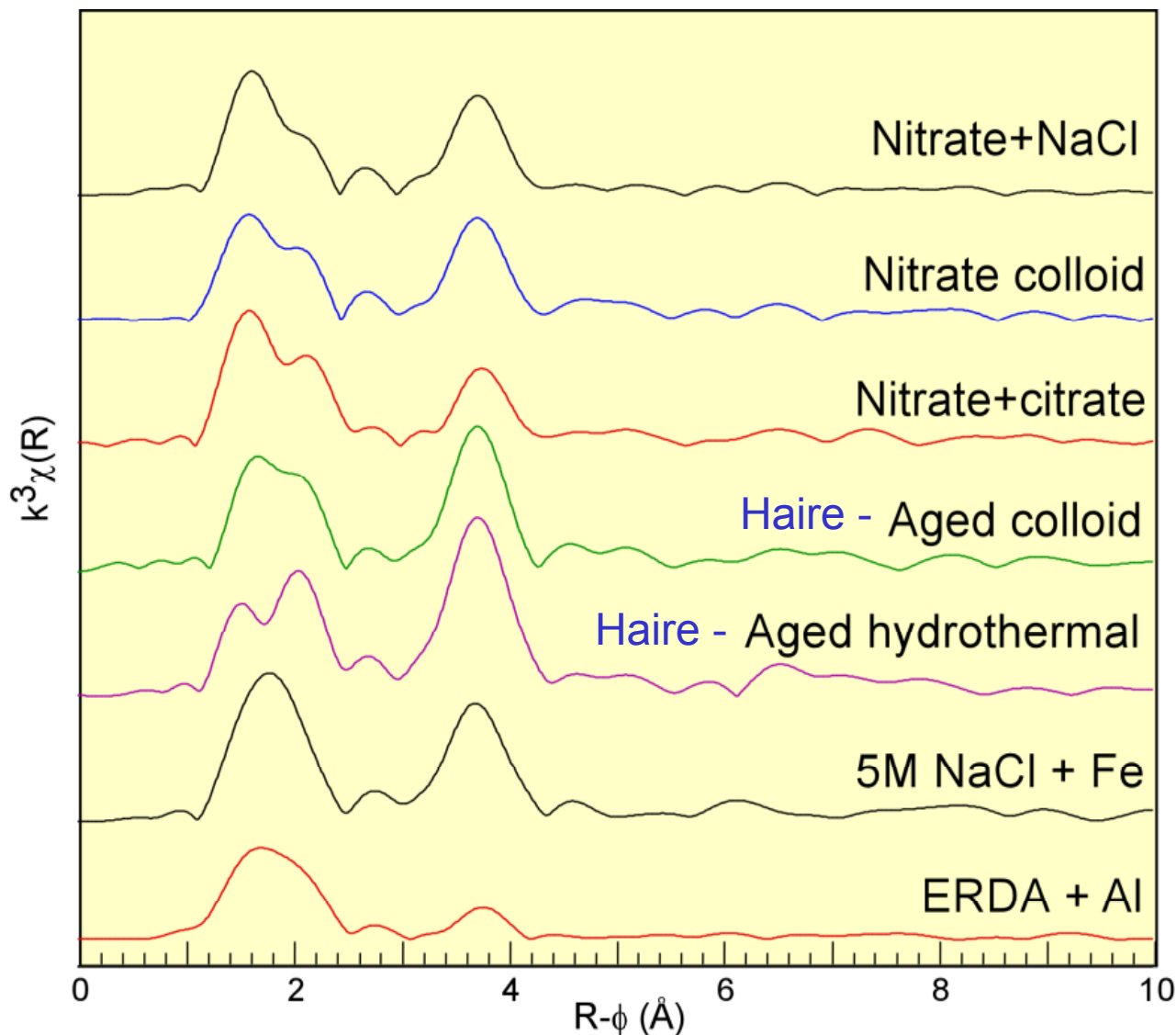
Systematic XAS Study of PuO_{2+x} Formation



- High temperature (300 °C) reaction conditions
- Characterized by PVT, TGA, MS, and XRD techniques
- All show fcc structures, similar a_0 by XRD
- diminished order with x , via Pu and O atom displacements
- Peak splitting of first O shell is related to x
- XANES - mixed valent IV/V solid

XAFS Studies of Colloidal precipitates

Pu(IV) colloidal precipitates from aqueous solution

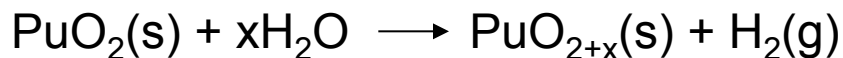


Key Features

- Intrinsic colloids, prepared under a wide variety of conditions (25°C)
- PuO_{2+x} and intrinsic Pu(IV) colloidal precipitates share structural similarity
- PuO_2 -like structural features

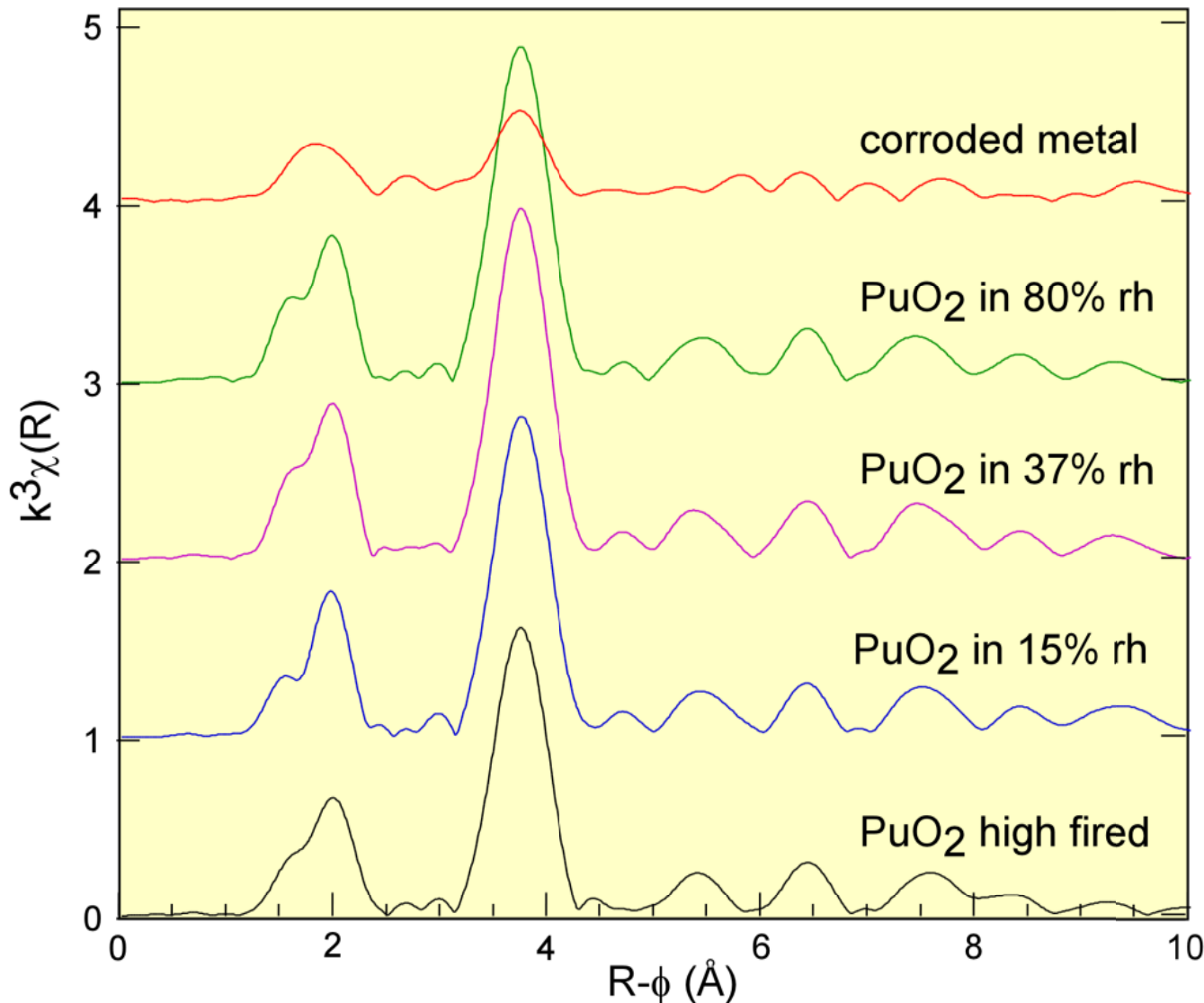
Conradson, et al, *J. Am. Chem. Soc.*, 2004, 126, 13443

Systematic XAS Studies of PuO_{2+x}



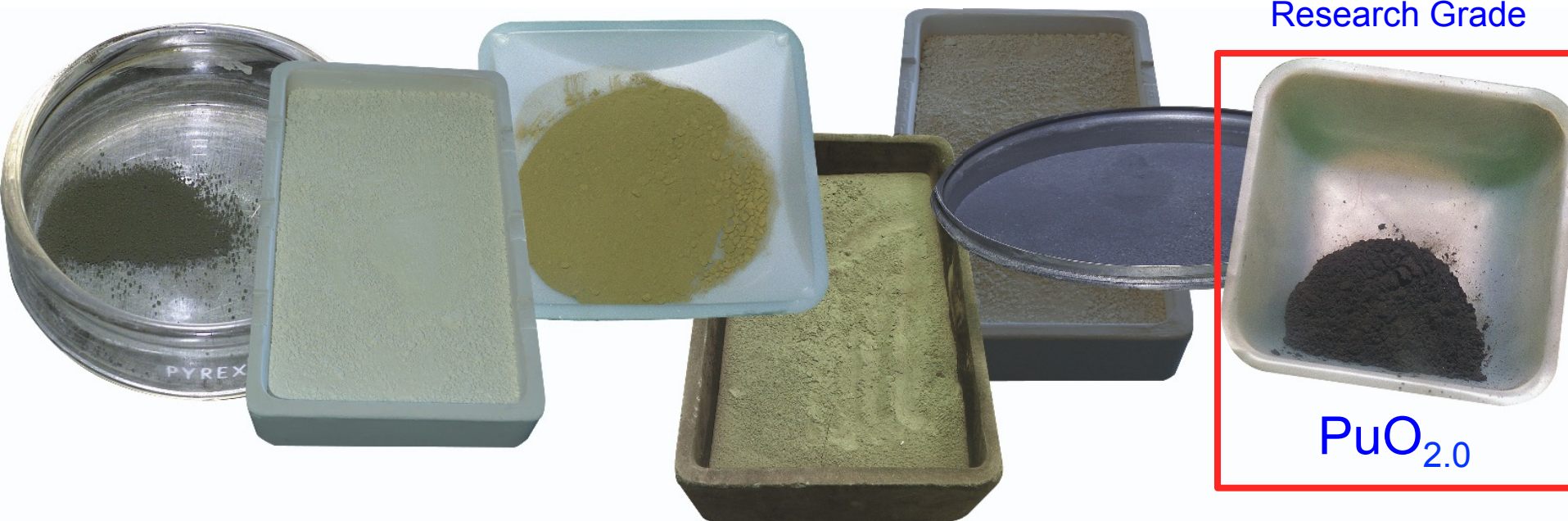
Key Features

- Ambient temperature (25°C) reaction conditions
- Characterized by PVT, TGA, MS, and XRD techniques
- Similar peak splitting and spectral features observed for ambient temperature exposure of PuO_2 to H_2O



Will the real PuO_2 please step forward?

- Legendary variability in color and general appearance for samples of PuO_2
- PuO_2 is normally olive green, but samples of yellow, buff, khaki, tan, slate, and black are also common – all show similar XRD and a_0
- Which of these is PuO_2 and which is PuO_{2+x} ?

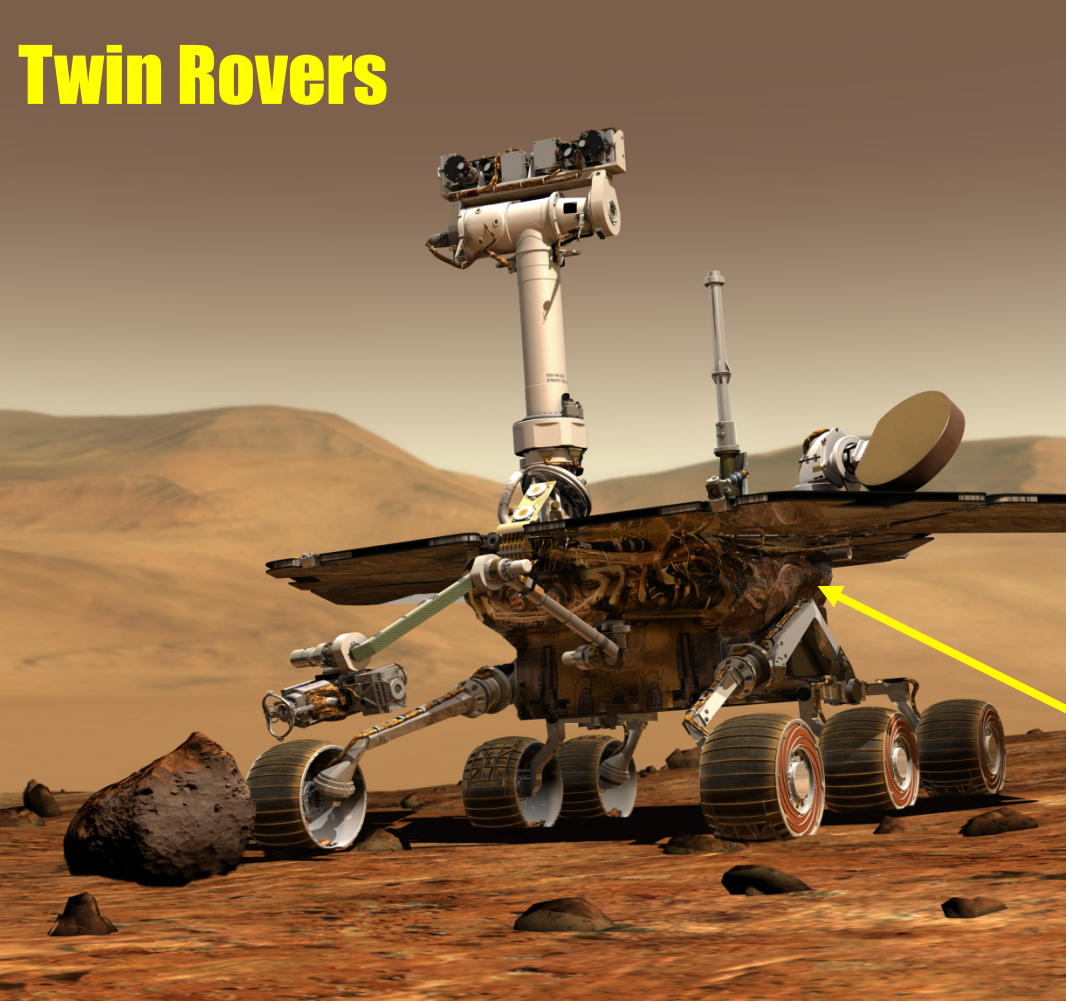


$^{238}\text{PuO}_2$ – Heat for Mars Rovers

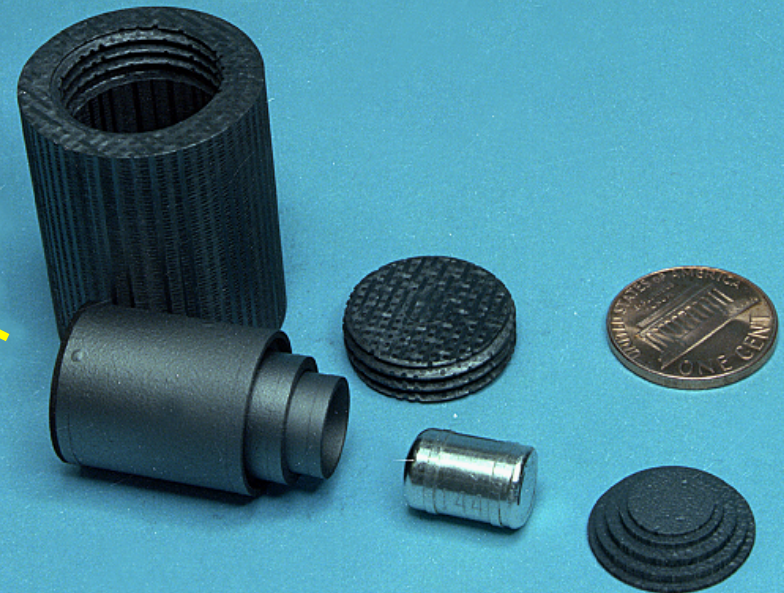
Pathfinder



Twin Rovers

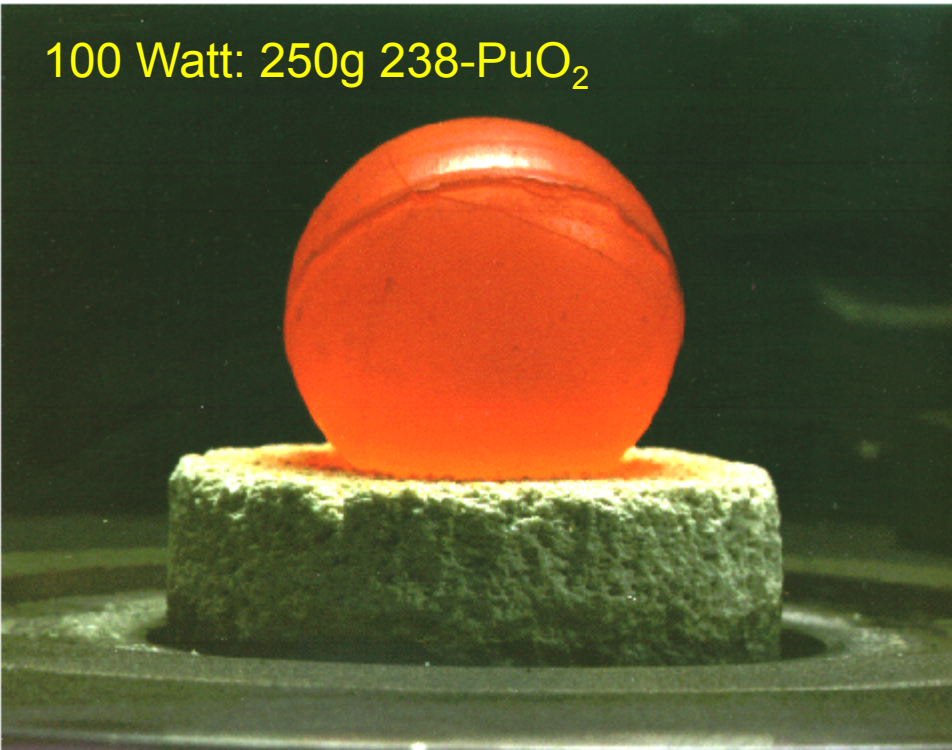


8 LWRHUs
2.7g $^{238}\text{PuO}_2$ 1 Watt

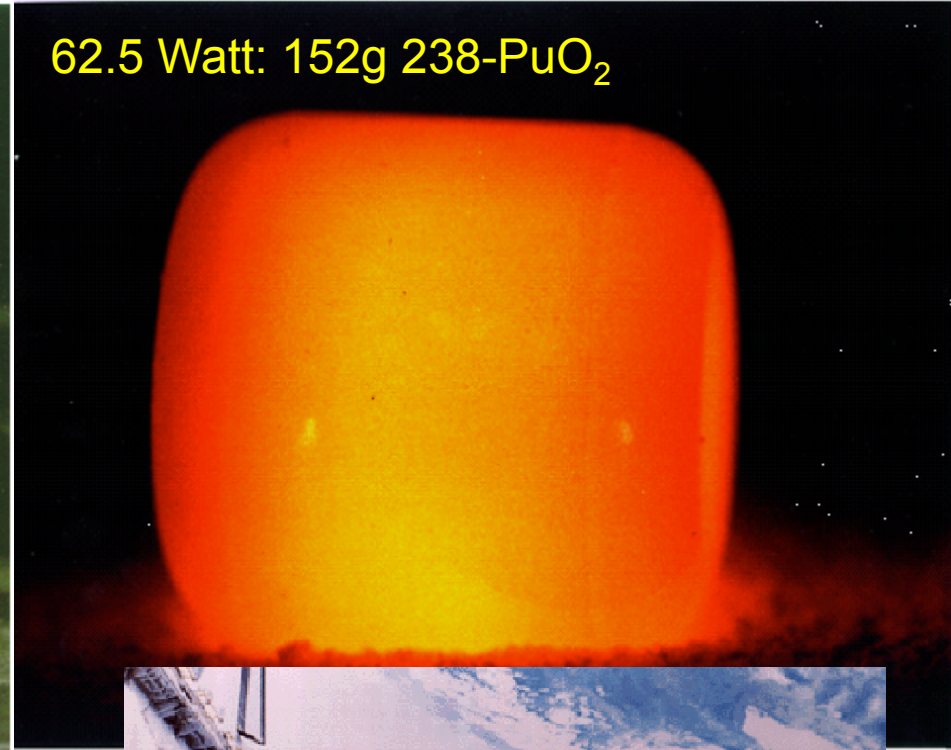


Space Exploration - Power Source Technologies

100 Watt: 250g $^{238}\text{PuO}_2$



62.5 Watt: 152g $^{238}\text{PuO}_2$

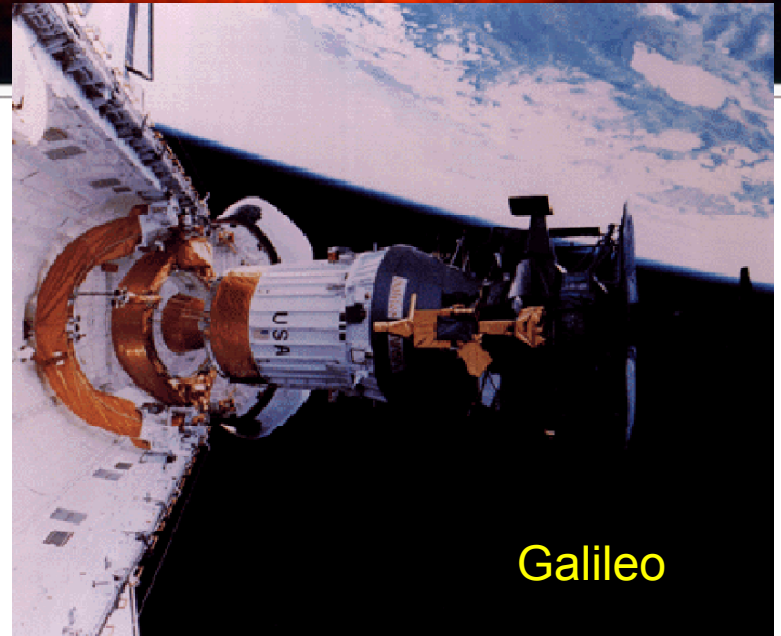


General Purpose
Heat Source - GPHS

Iridium frit vent



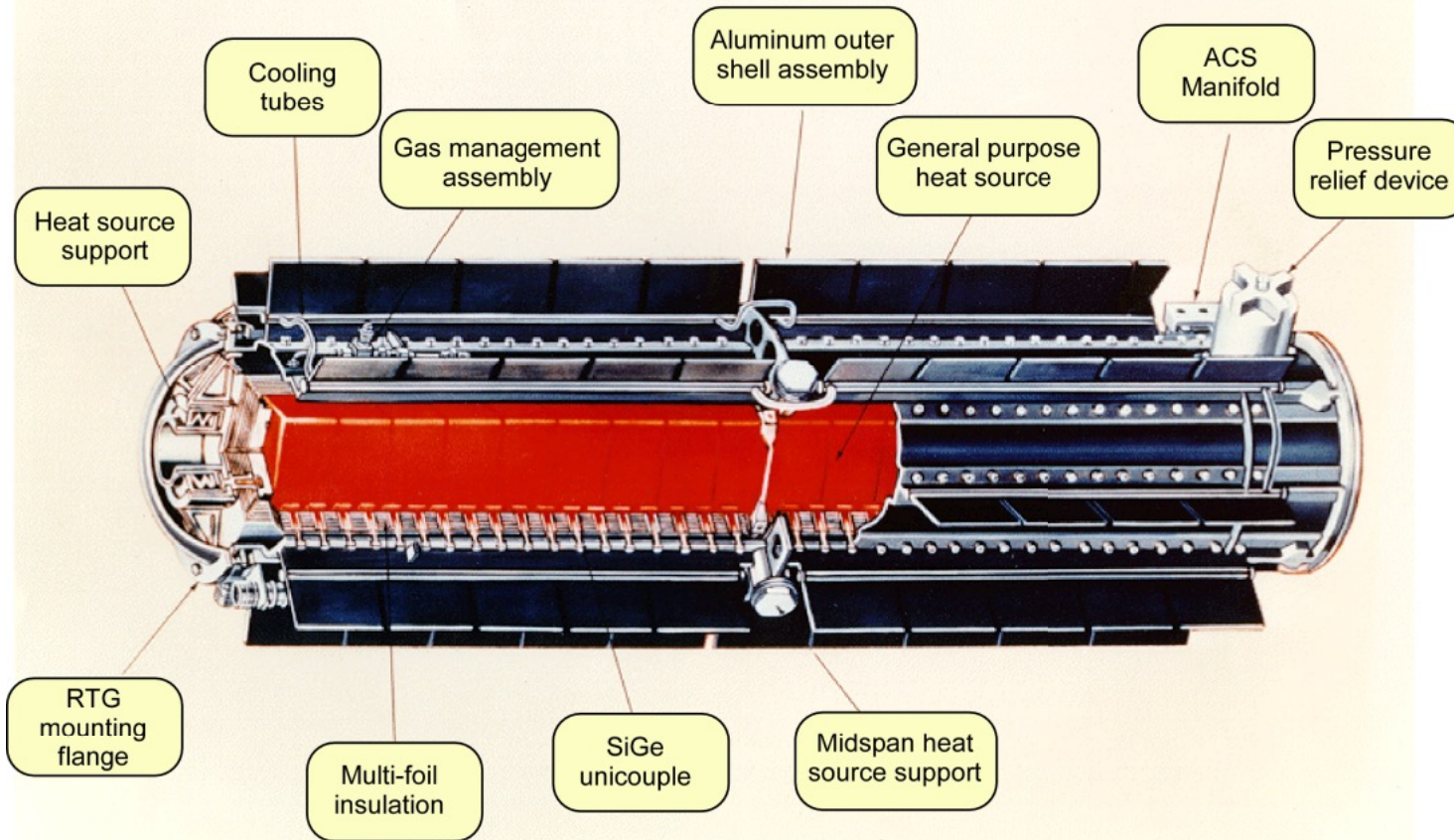
Iridium-clad capsule
equatorial Tungsten
arc weld



Galileo

Radioisotope Thermoelectric Generator

GPHS - RTG



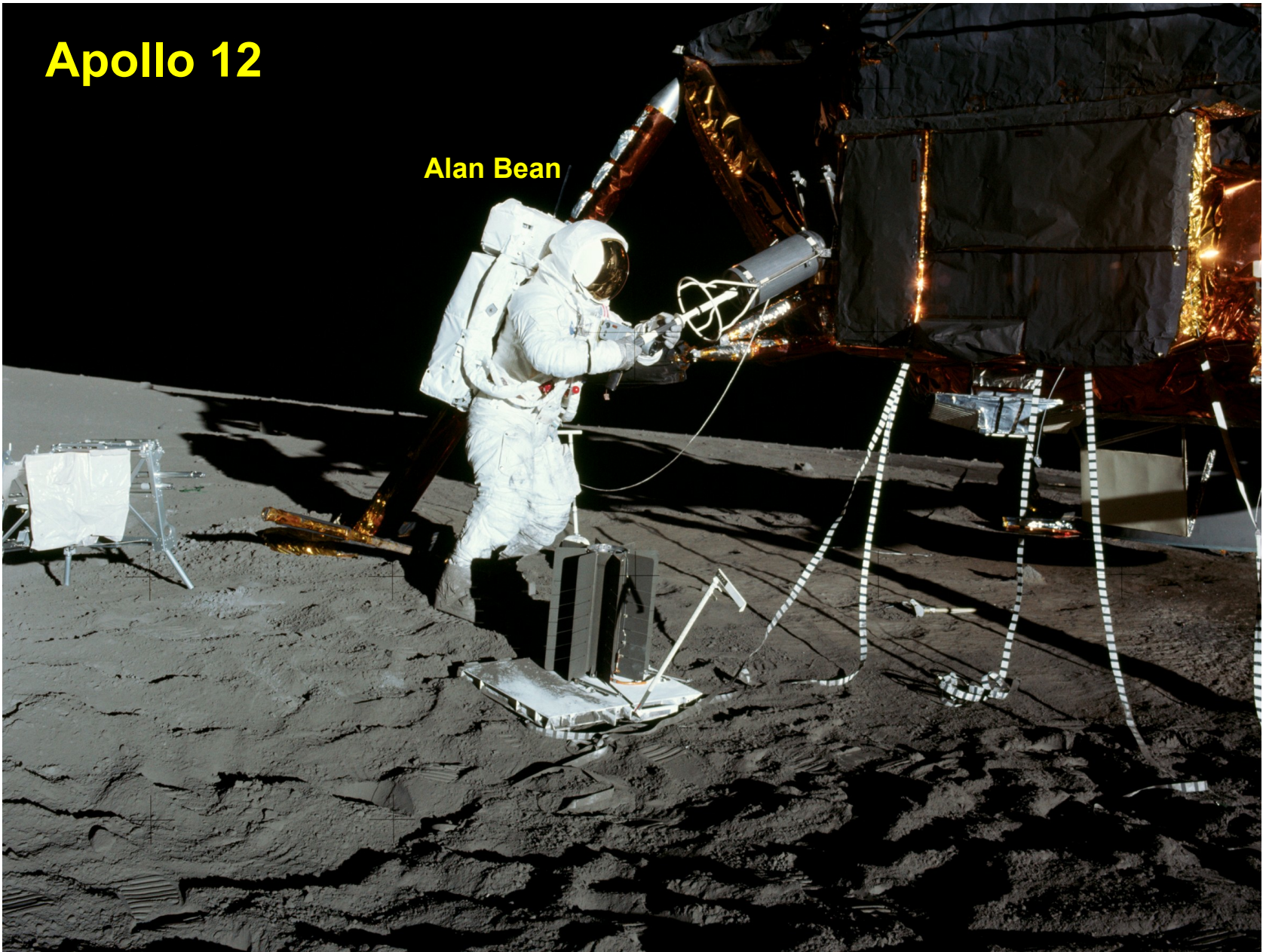
- 2 GPHS pellets per impact shell
- 2 impact shells per module
- 18 modules per RTG
- Total 72 GPHS pellets per RTG
- 24 lbs (11 kg) Pu
- 200 Watts power

Apollo Lunar Surface Experiment Package (ALSEP)

20

Apollo 12

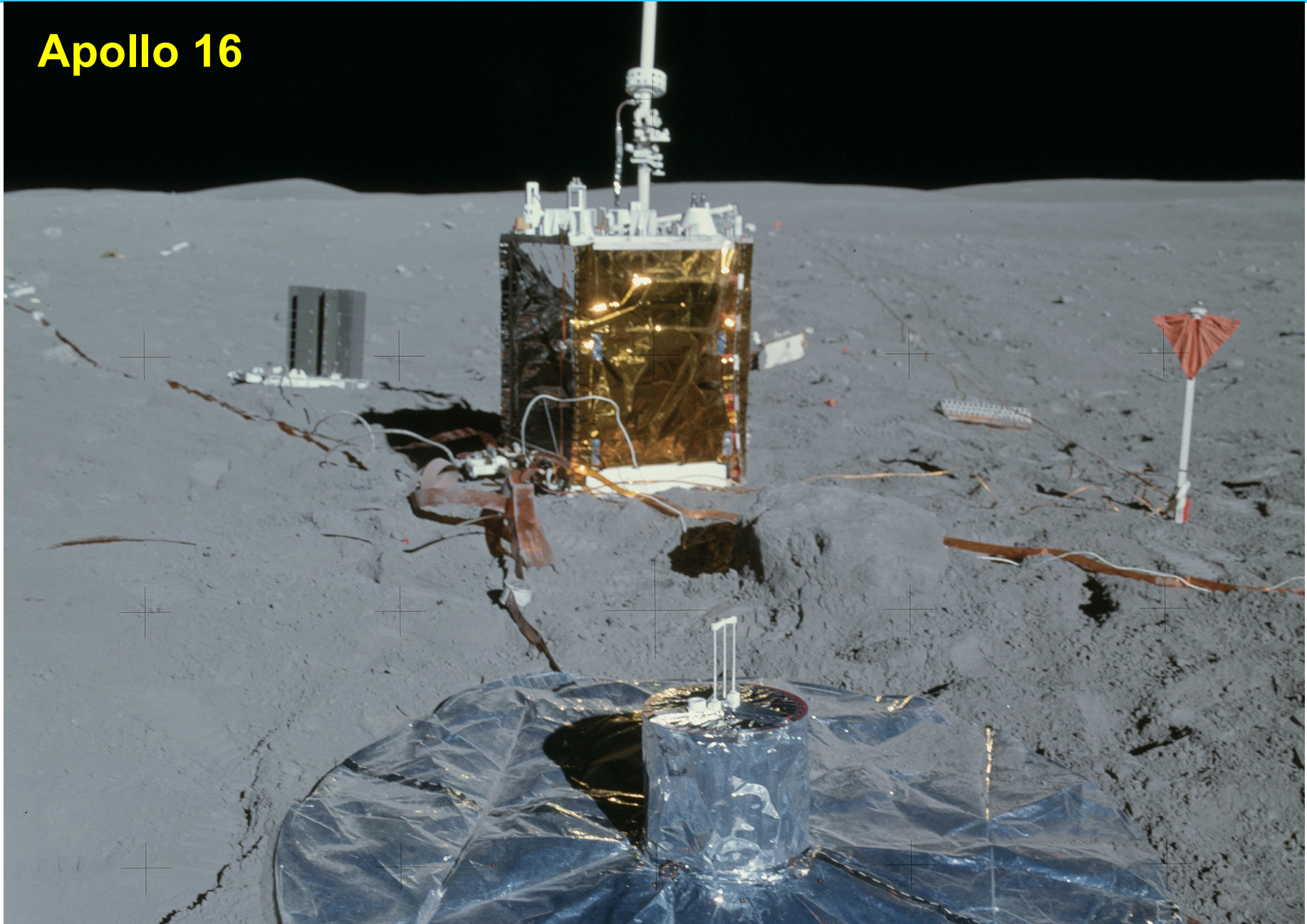
Alan Bean



Apollo Lunar Surface Experiment Package (ALSEP)

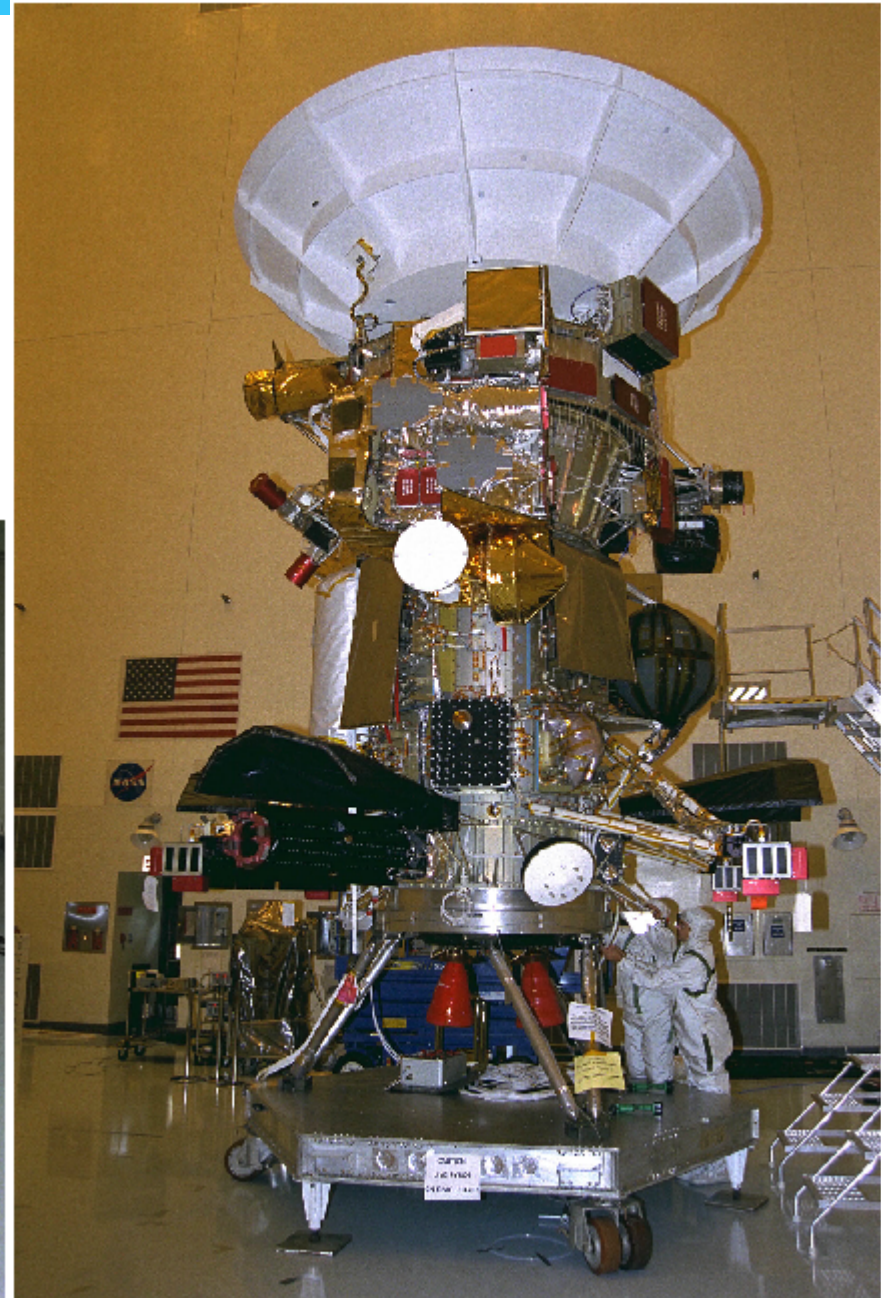
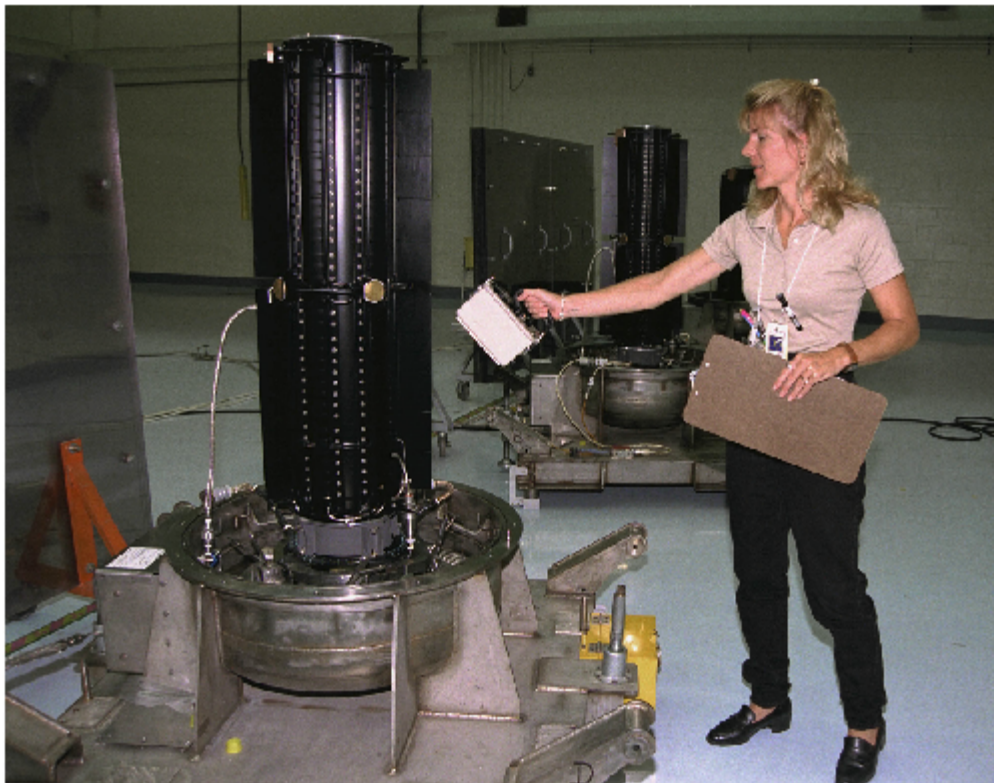
21

Apollo 16



Cassini Heat and Power Sources

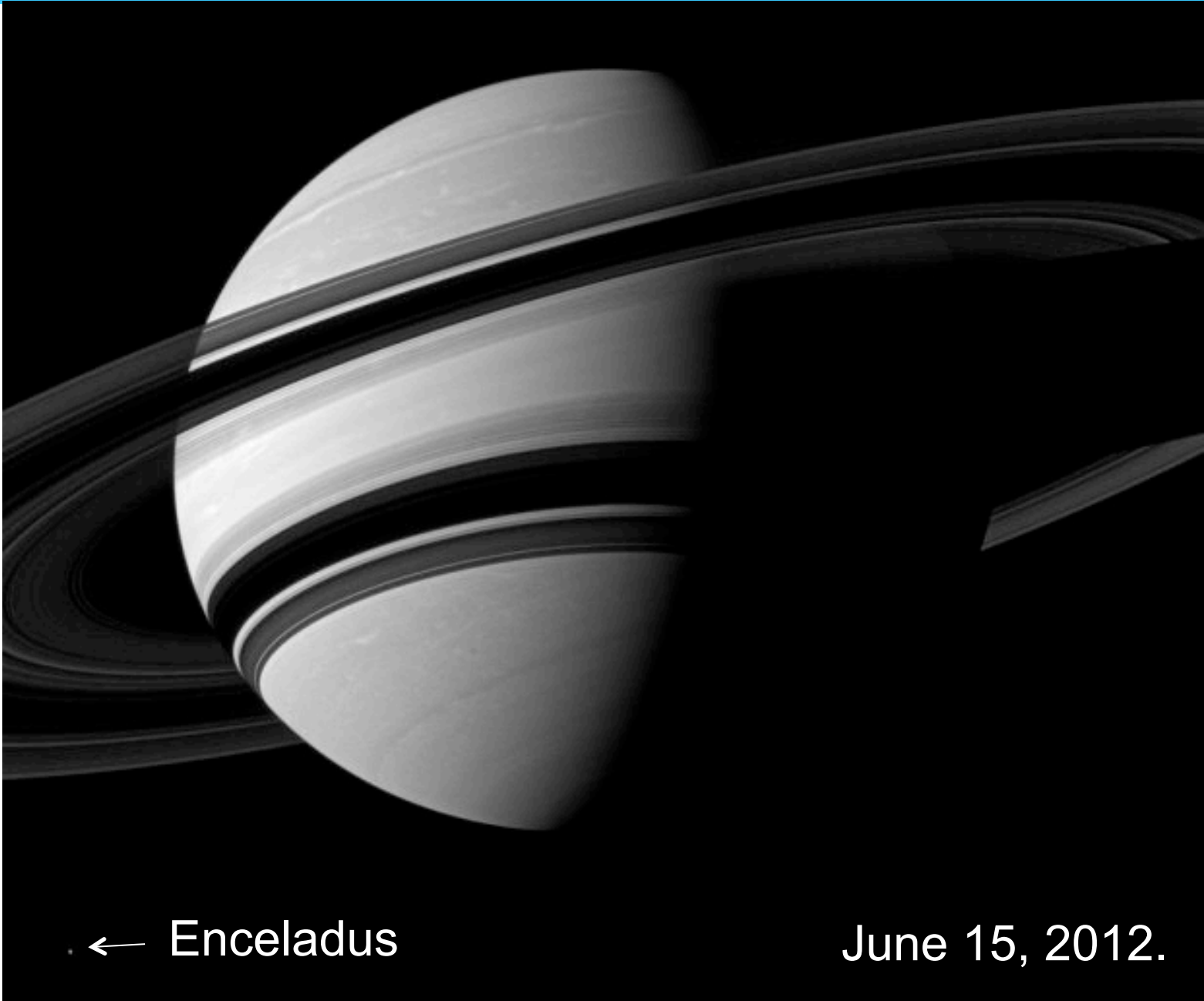
- 333 LANL Heat Sources
- 117 RHUs (0.7 lbs)
 - heat for spacecraft components
- 216 GPHS pellets (72 lbs)
 - electrical power



Jupiter Flyby



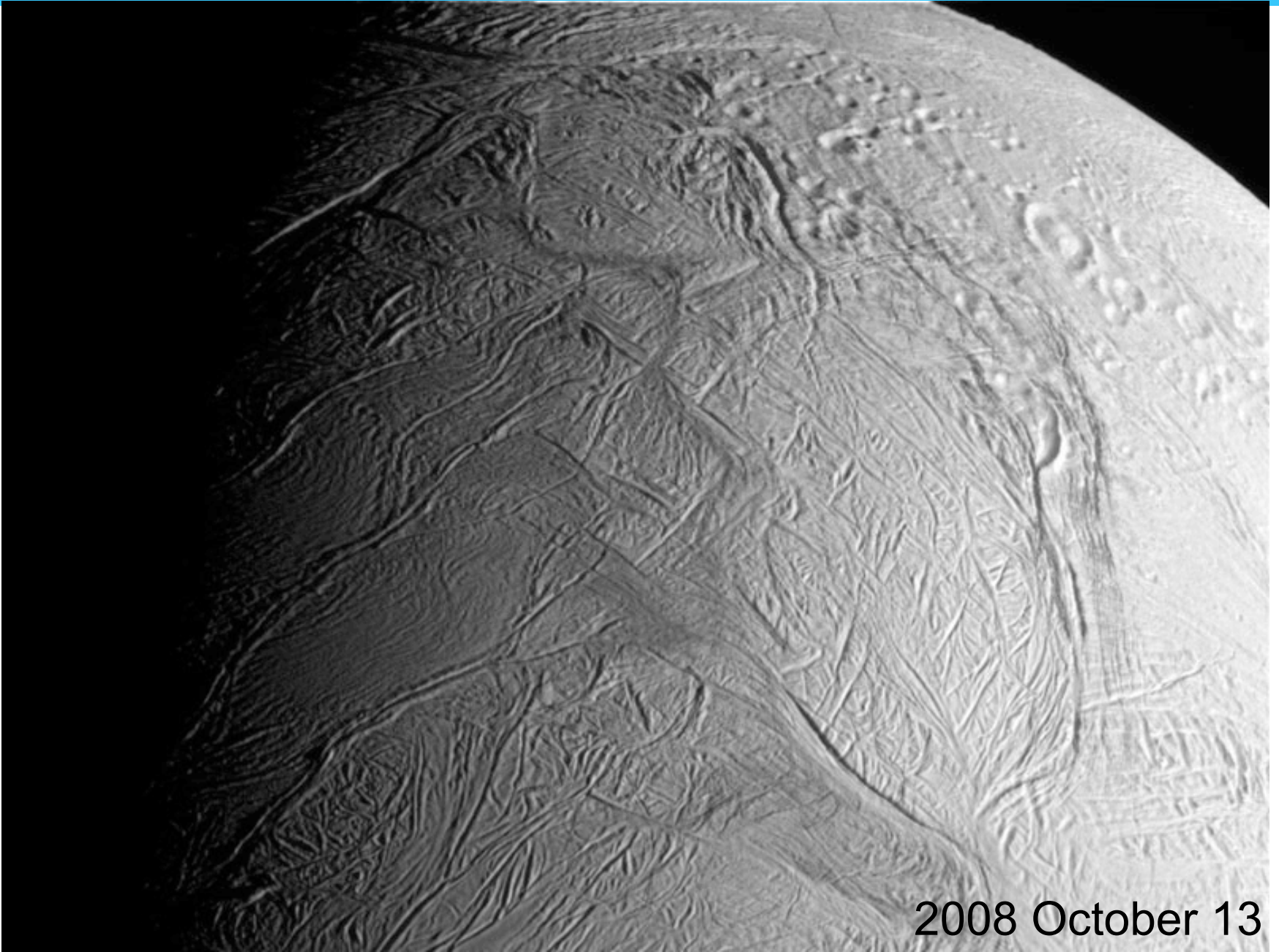
Cassini Studies Saturn



← Enceladus

June 15, 2012.

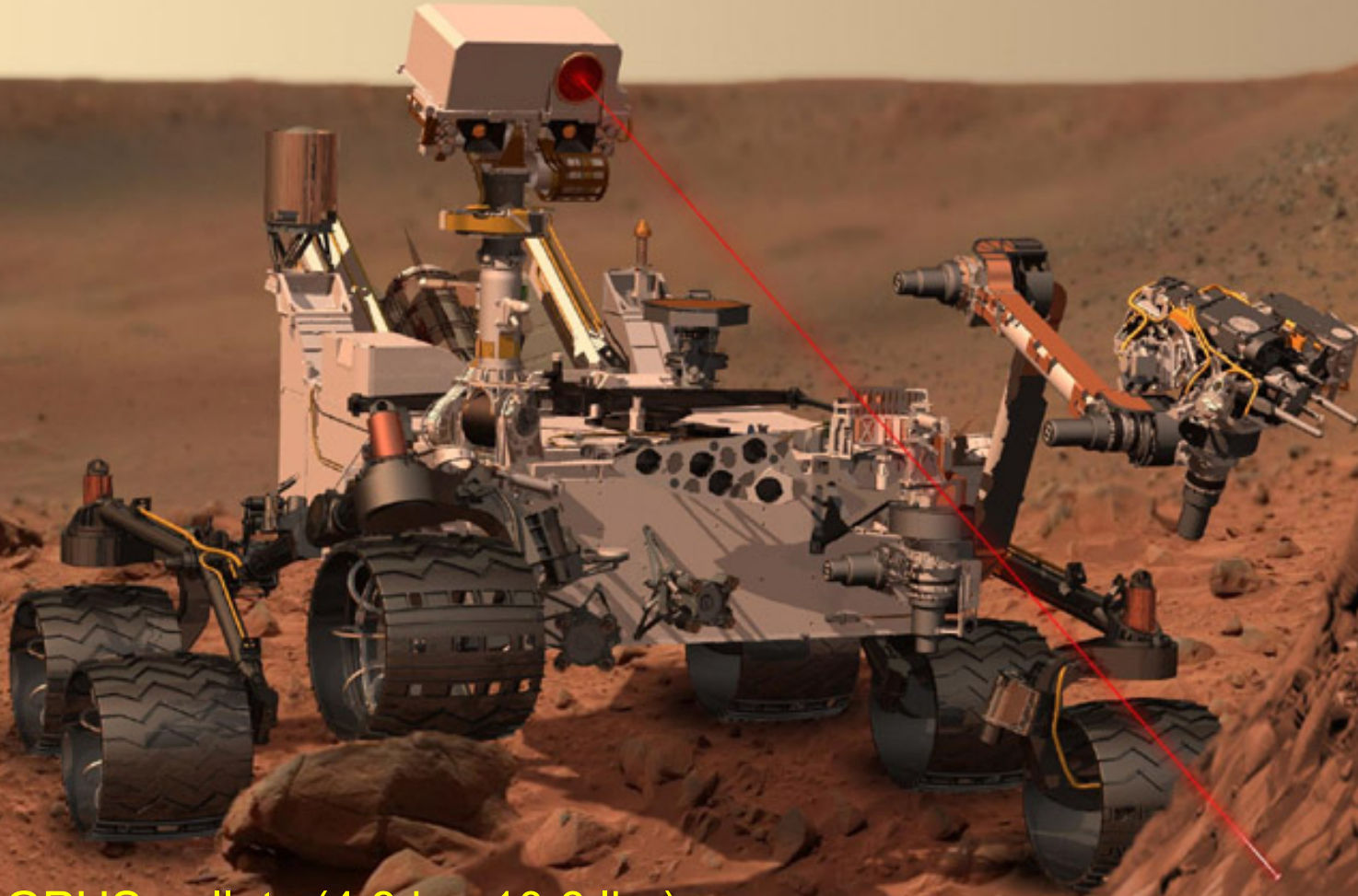
Ice Plumes of Enceladus



2008 October 13

Curiosity Heat and Power Sources

- 125 watts of electrical power from 2000 watts of thermal power at start of the mission.
- The Mars Sci Laboratory will generate 2.5 kilowatt hrs per day



32 GPHS pellets (4.8 kg, 10.6 lbs)

New Horizons Pluto-Kuiper Belt Mission

61 GPHS pellets
1 RTG, 170 Watts

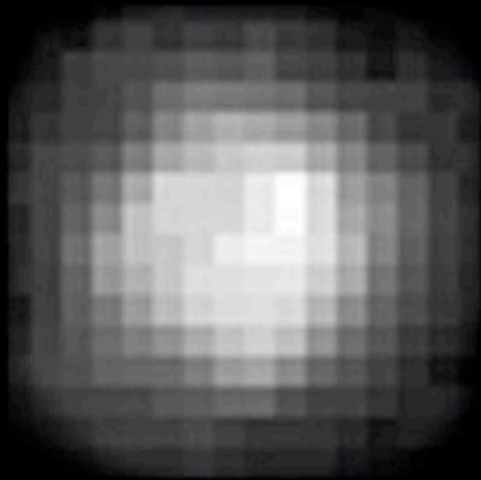
24 lbs plutonium
Arrival July 14, 2015



New Horizons Pluto-Kuiper Belt Mission

Science

Pluto



1996



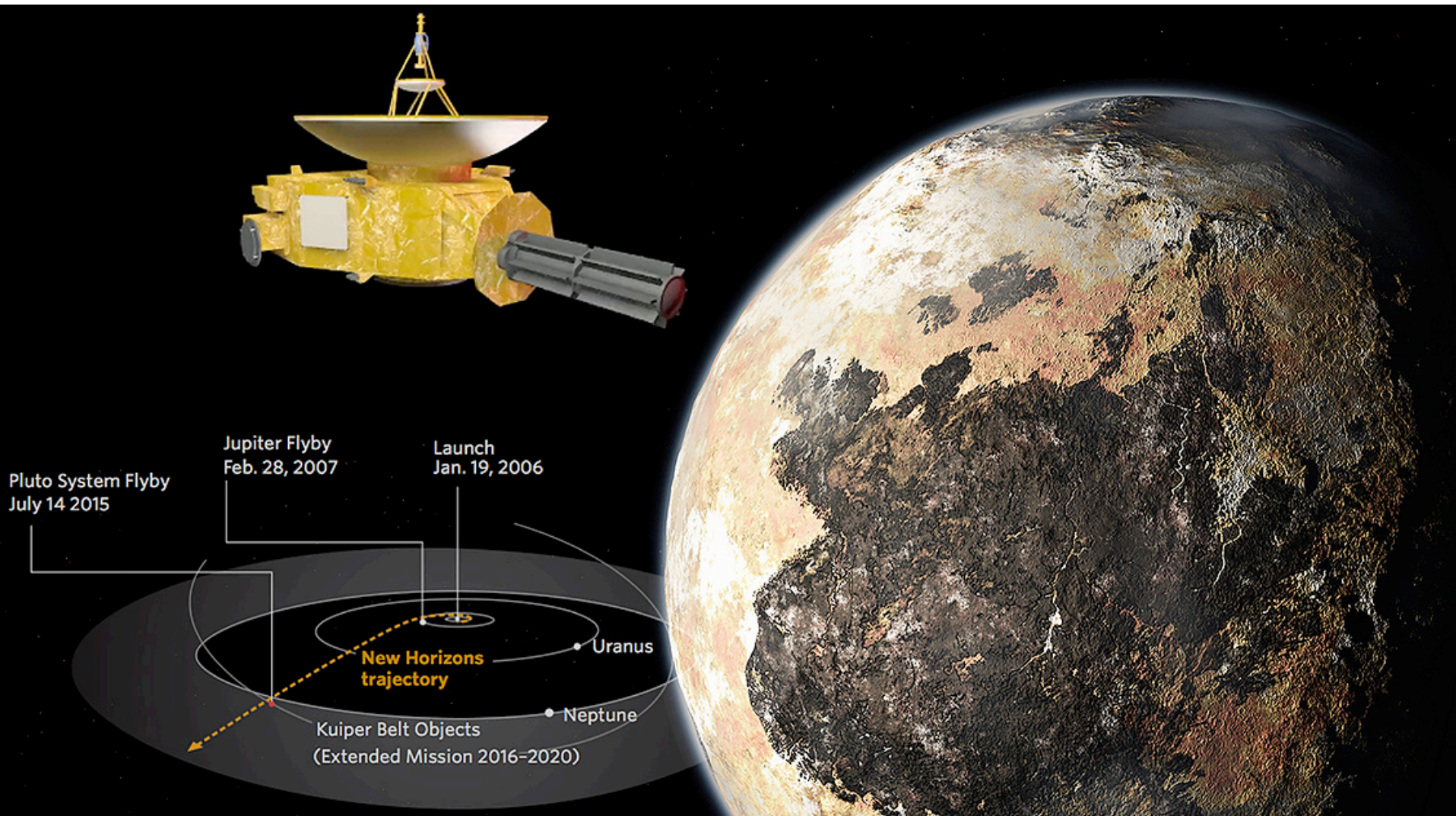
2005



2015

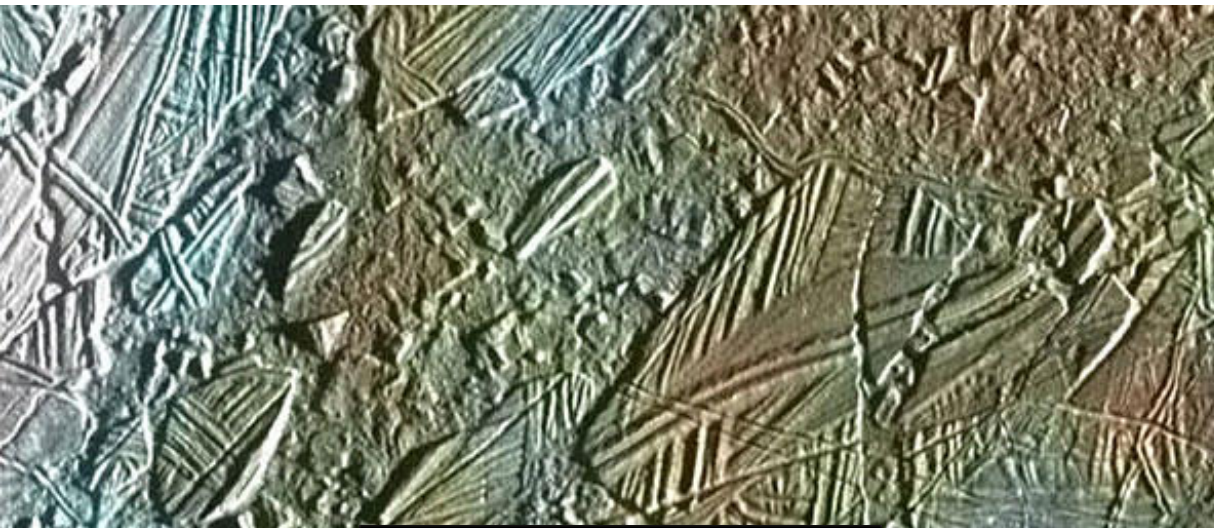
Credits(left to right): Alan Stern (Southwest Research Institute), Marc Buie (Lowell Observatory) NASA and ESA; NASA, ESA, H. Weaver (JHU/APL), A. Stern (SwRI), and the HST Pluto Companion Search Team; NASA/APL/SwRI

New Horizons Pluto-Kuiper Belt Mission



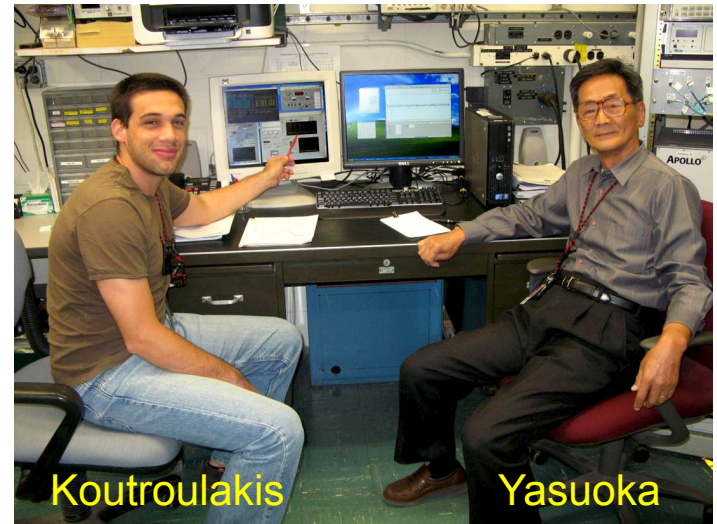
Plutonium power enabled decadal science

Europa: secret lakes could fuel life on Jupiter moon



In Search of the ^{239}Pu NMR transition

- NMR has revolutionized chemistry, physics, and medicine by observation of matter at atomic scales
- Every spin-1/2 nucleus had been studied by NMR except ^{239}Pu
- For over 50 years, chemists and physicists have been searching for its signal
- LANL chemists and physicists assembled an international team (LANL, JAEA) for first observation of ^{239}Pu
- Visiting Seaborg Scholar Hiroshi Yasuoka, JAEA



Koutroulakis

Yasuoka

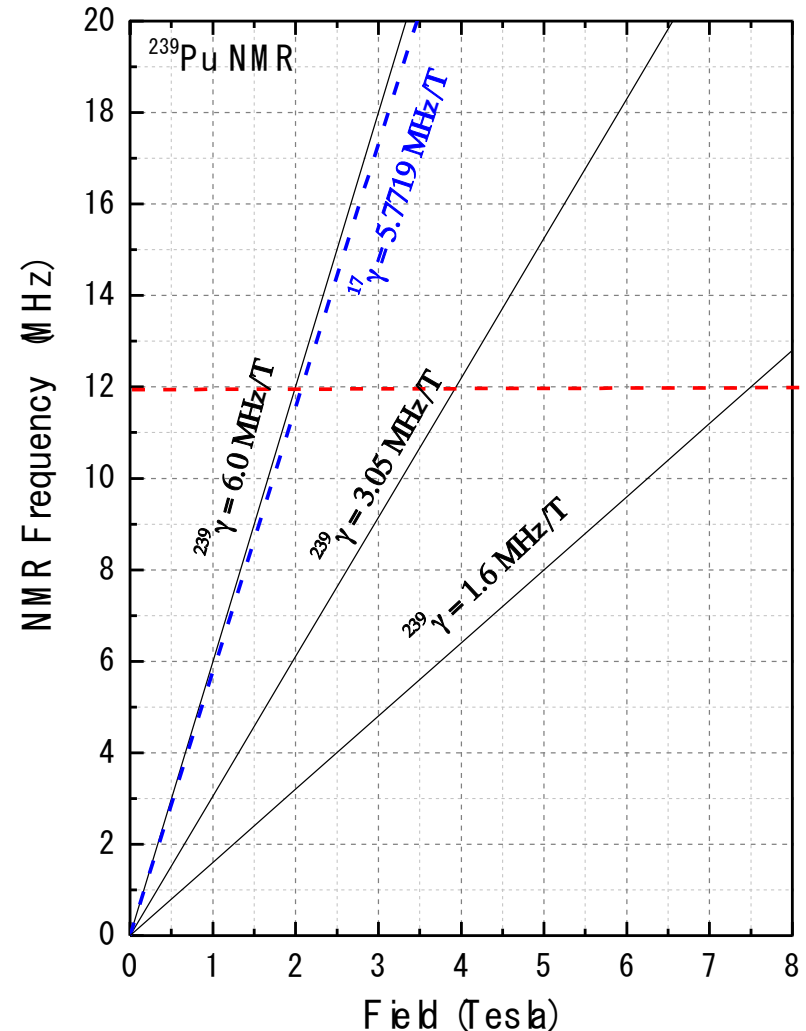
Why has ^{239}Pu NMR been elusive?

- Localized 5f-electron creates a **strong hyperfine interaction** and leads to very **large internal magnetic field** at the nuclear site.
- Then, it has extremely short T_1 .

$\text{Pu}^{3+} (5f^5) : \Gamma_6$ magnetic ground state

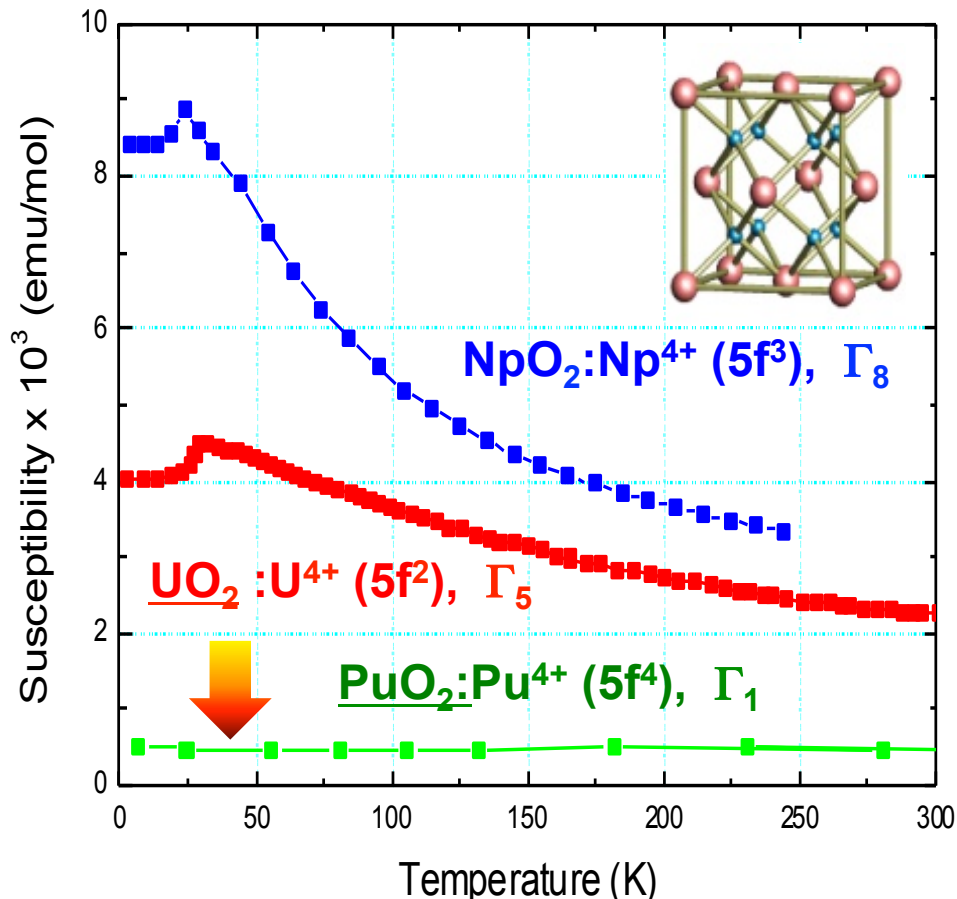
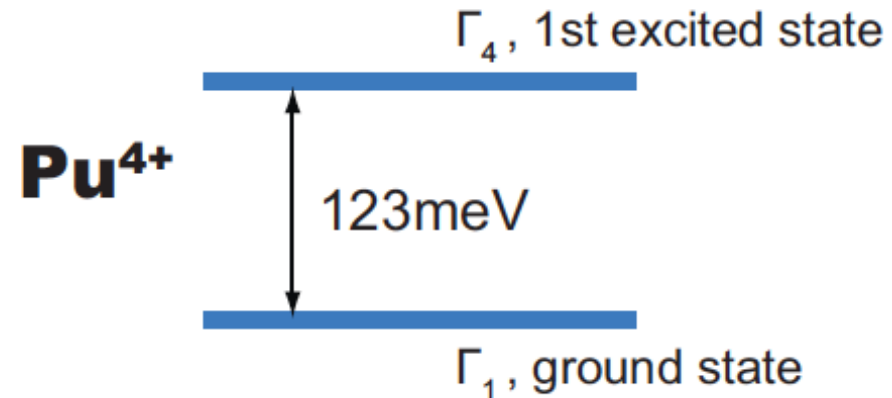
$\text{Pu}^{4+} (5f^4) : \Gamma_1$ nonmagnetic singlet

- The value of nuclear moment (γ_n) for ^{239}Pu had not been determined leading to a large parameter space



Favorable magnetic properties for ^{239}Pu NMR

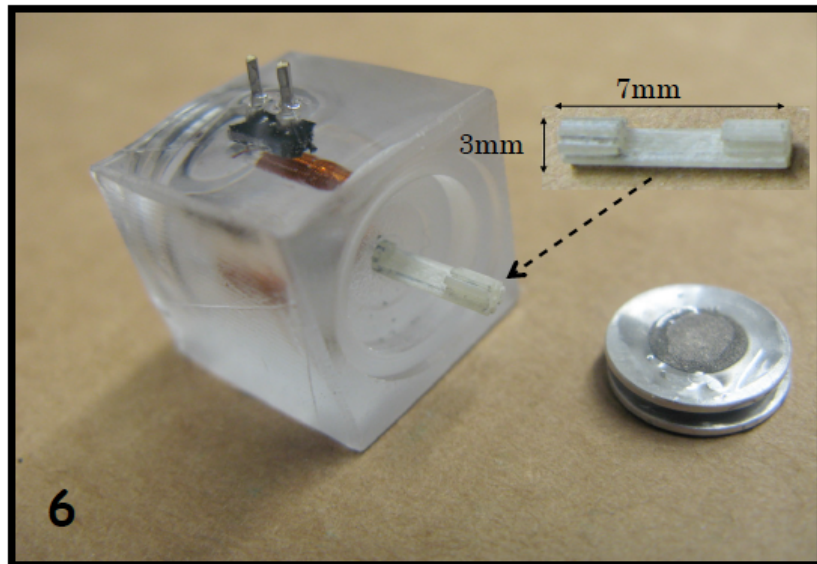
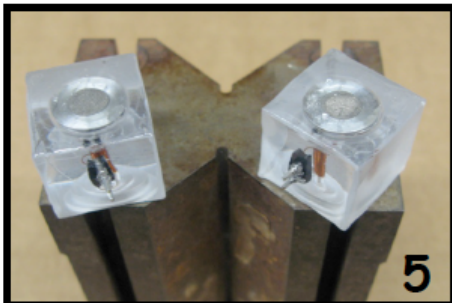
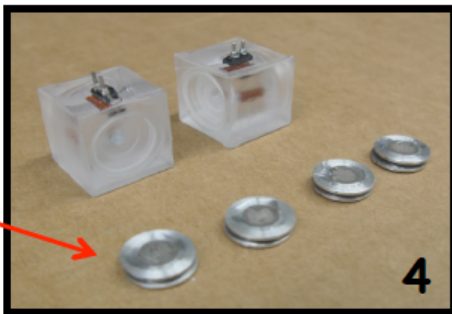
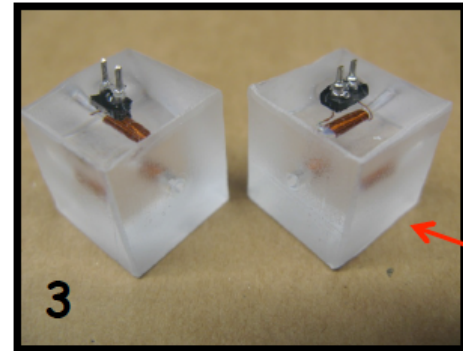
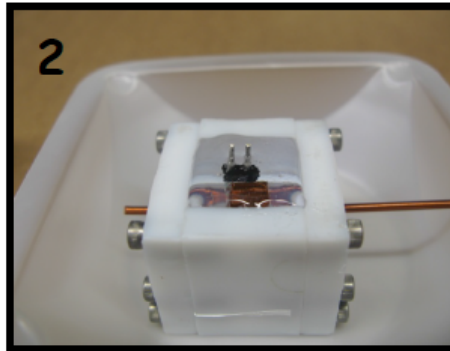
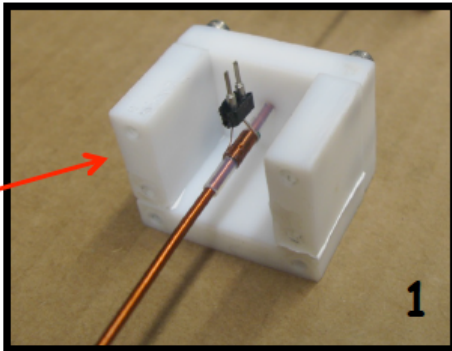
- When fully oxidized, PuO_2 should have Pu^{4+} ($5f^4$, $^3\text{H}_4$) with a singlet ground state, with excited state 123 meV higher



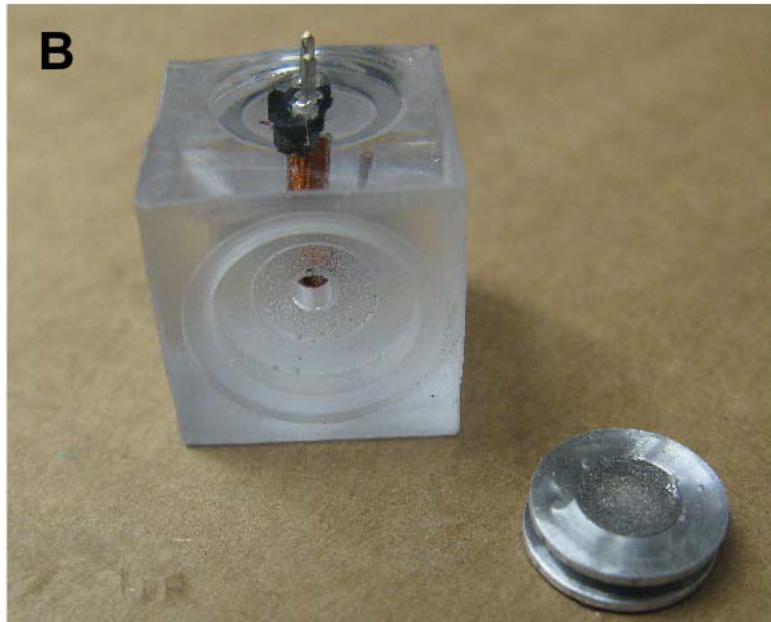
- PuO_2 should be nearly non-magnetic at Low T
- T-dependent Van-Vleck susceptibility
- $\chi_0 = 5.36 \times 10^{-4} \text{ emu/mol}$

Sample encapsulation for Pu NMR experiments

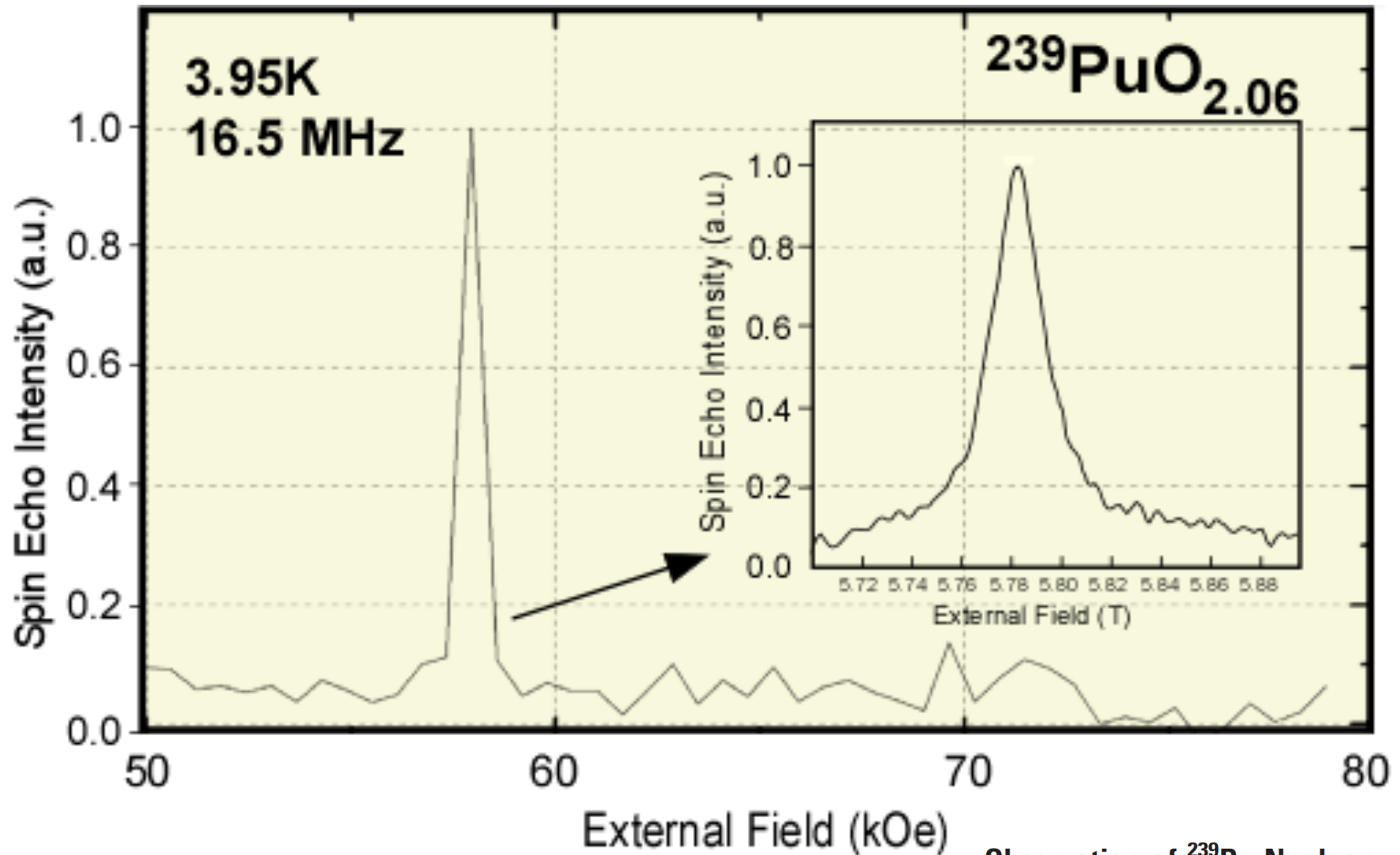
High purity PuO_2 powder (50 mg) with 94% isotopic purity ^{239}Pu
Encapsulated to prevent contamination



Sample encapsulation for Pu NMR experiments



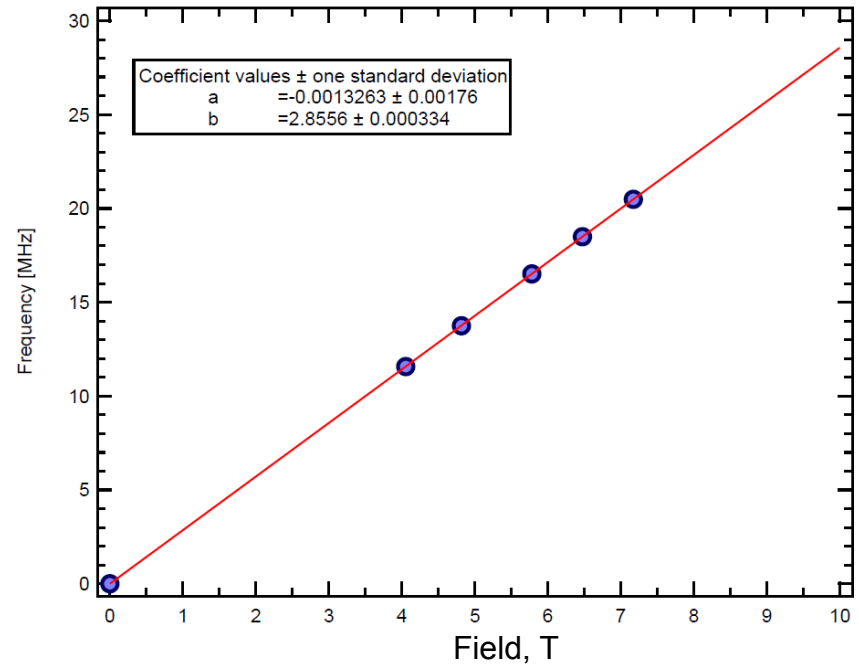
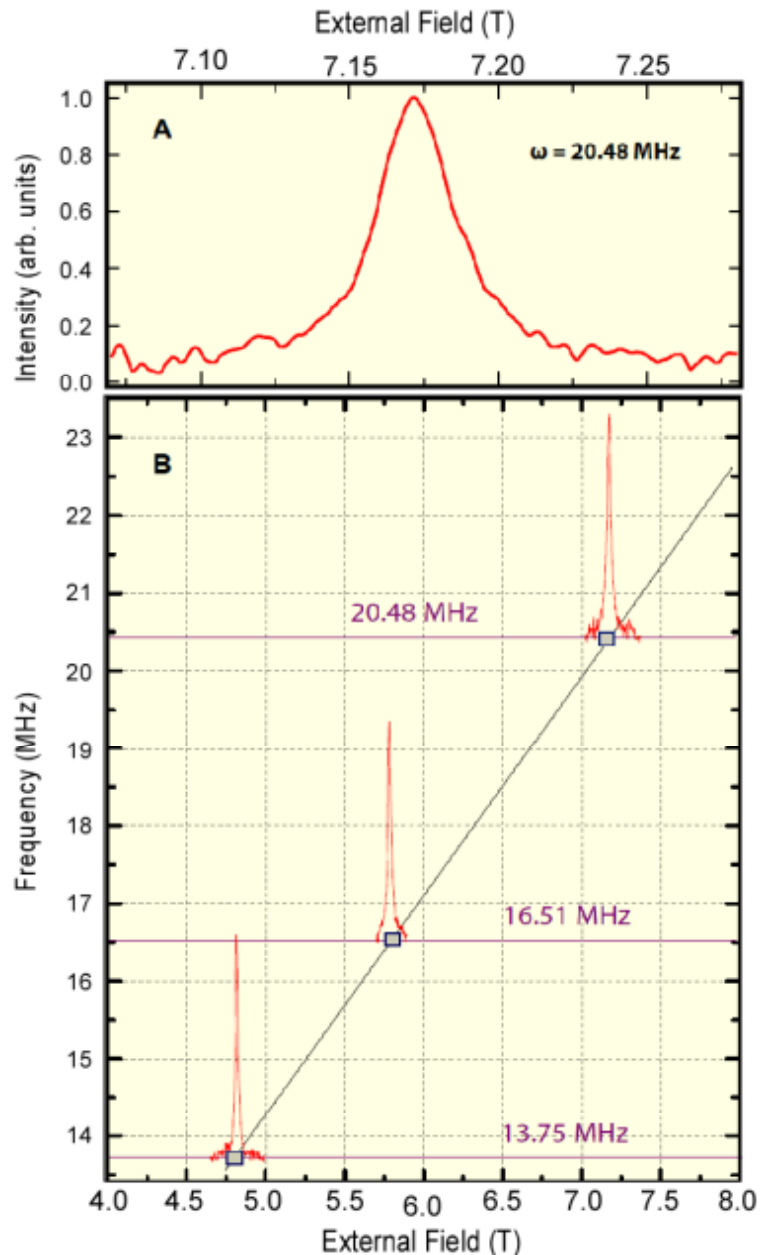
The First Observation of ^{239}Pu NMR transition



Observation of ^{239}Pu Nuclear Magnetic Resonance

H. Yasuoka,^{1,2} G. Koutroulakis,^{1*} H. Chudo,^{1,2} S. Richmond,¹ D. K. Veirs,¹ A. I. Smith,¹ E. D. Bauer,¹ J. D. Thompson,¹ G. D. Jarvinen,¹ D. L. Clark²

Nuclear Gyromagnetic Ratio of ^{239}Pu in PuO_2



$$\nu_o = 16.51 \text{ MHz}, H_o = 5.783 \text{ T}$$

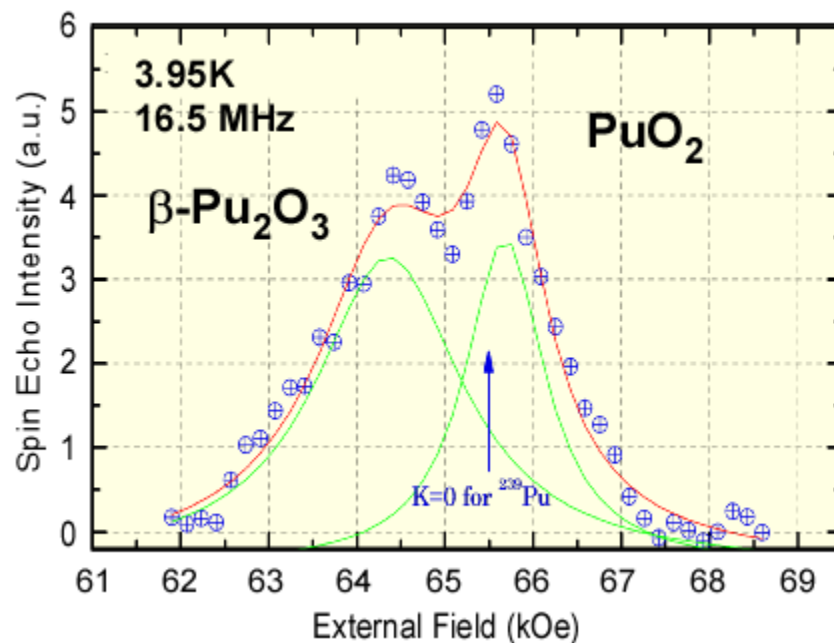
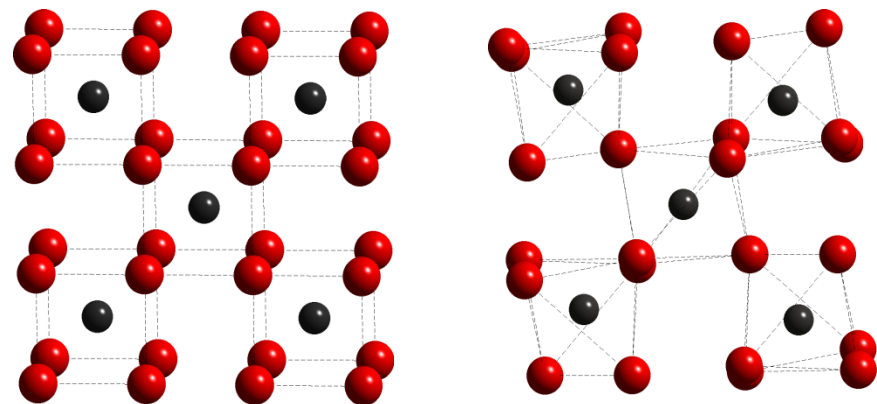
$$FWHM = 270 \text{ Oe}, T_1 \approx 10 \text{ sec}$$



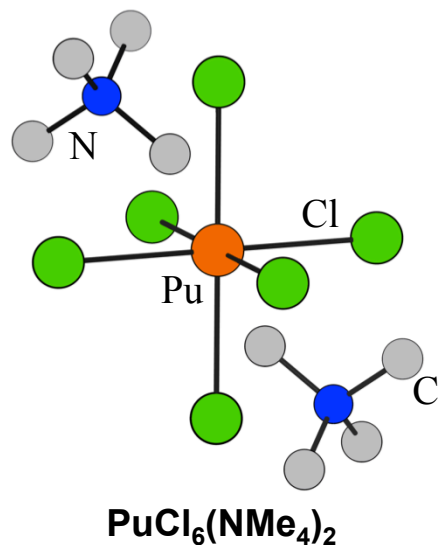
$$\frac{{}^{239}\gamma_n(\text{PuO}_2)}{2\pi} = 2.856 \pm 0.001 \text{ MHz/T}$$

H. Yasuoka *et al.* Science 336 901 (2012)

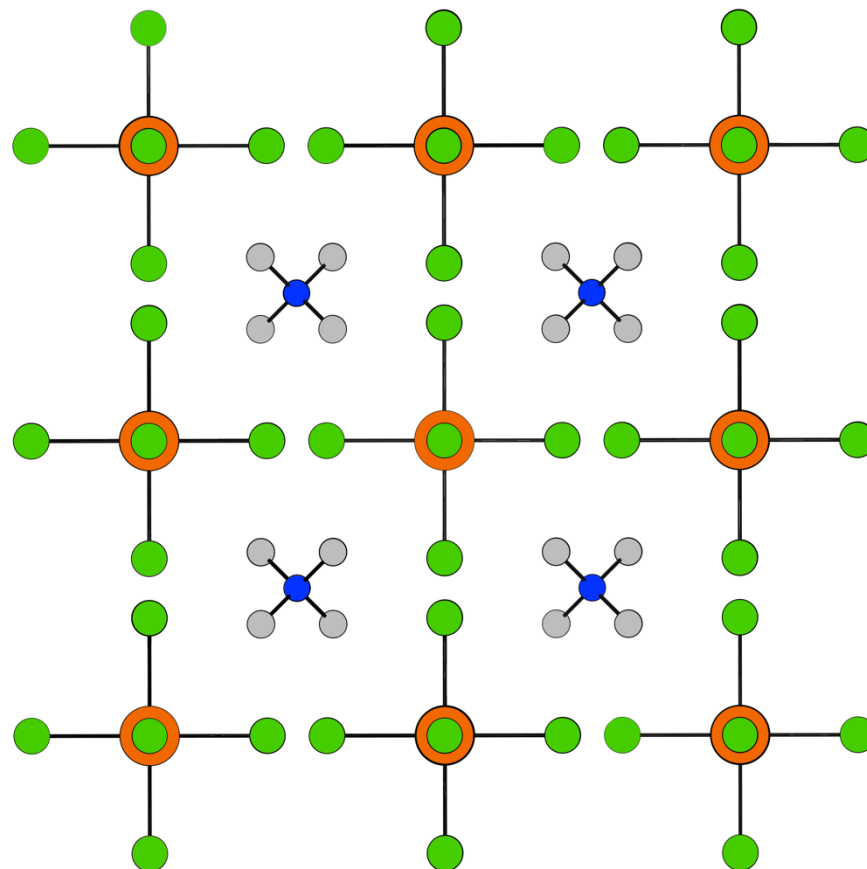
- High purity PuO_2 is not the only Pu compound that can be observed by $^{239}\text{-Pu}$ NMR
- Mixture of Pu_2O_3 and PuO_2 shows two signals for two chemical environments
- New collaborative proposal has been submitted to DOE OBES to explore the utility of the technique
- Ability to probe local structure of $^{239}\text{-Pu}$ in molecules, compounds, alloys could revolutionize the field



Search for ^{239}Pu NMR in $(\text{Me}_4\text{N})_2\text{PuCl}_6$



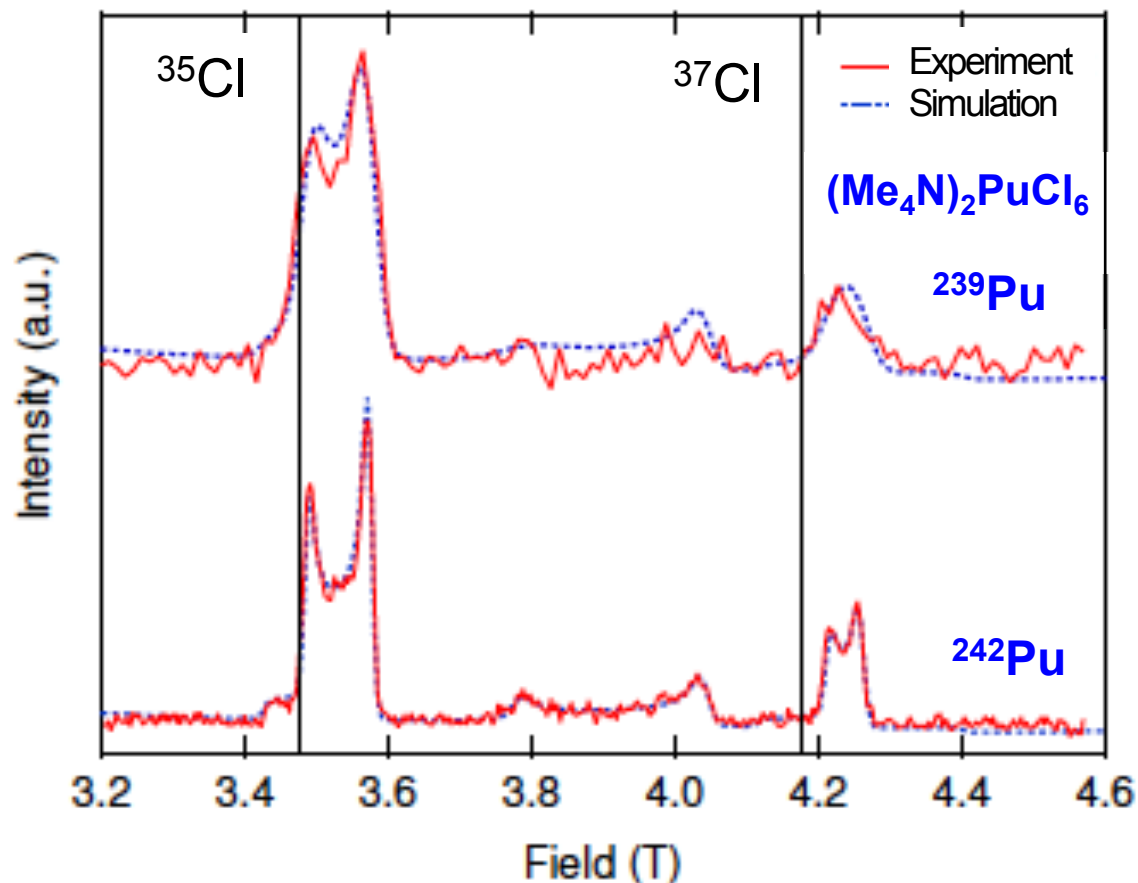
Mean Pu-Cl $2.59(1) \text{ \AA}$
 Mean Cl-Pu-Cl $90.5(8)^\circ$



- The $\text{PuCl}_6(\text{NMe}_4)_2$ salt crystallizes from solutions of HCl (6 M) in the cubic space group, which is exceptionally suited for Pu-239 NMR experiments.

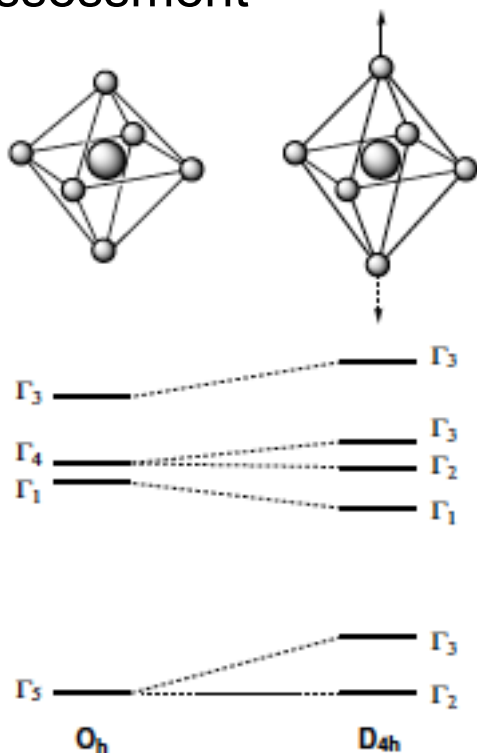
Search for ^{239}Pu NMR in $(\text{Me}_4\text{N})_2\text{PuCl}_6$

- Initial unidentified peak at ~ 3.6 T for ^{239}Pu sample
- ^{242}Pu sample (not NMR active) reveals spectrum only represent Cl resonance
- Resonant field for unshifted ^{35}Cl and ^{37}Cl are shown

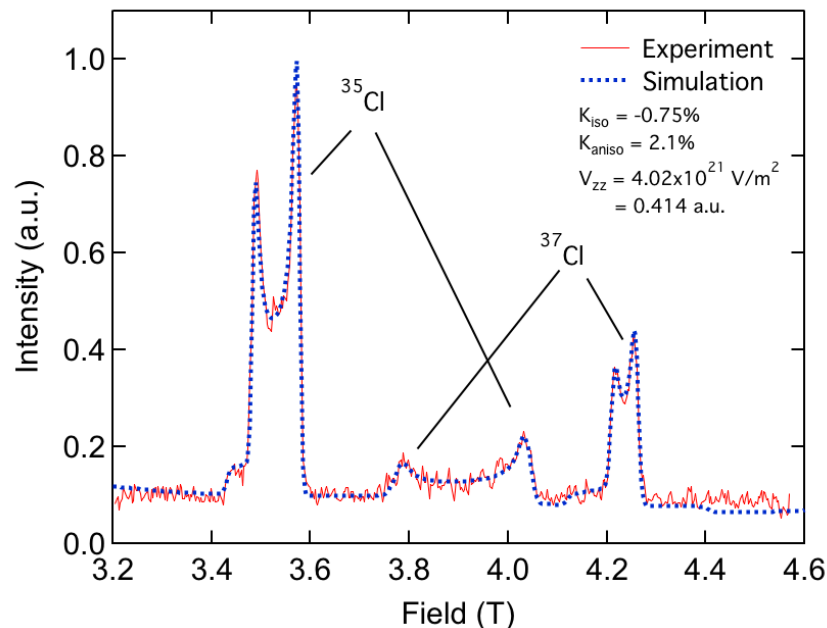
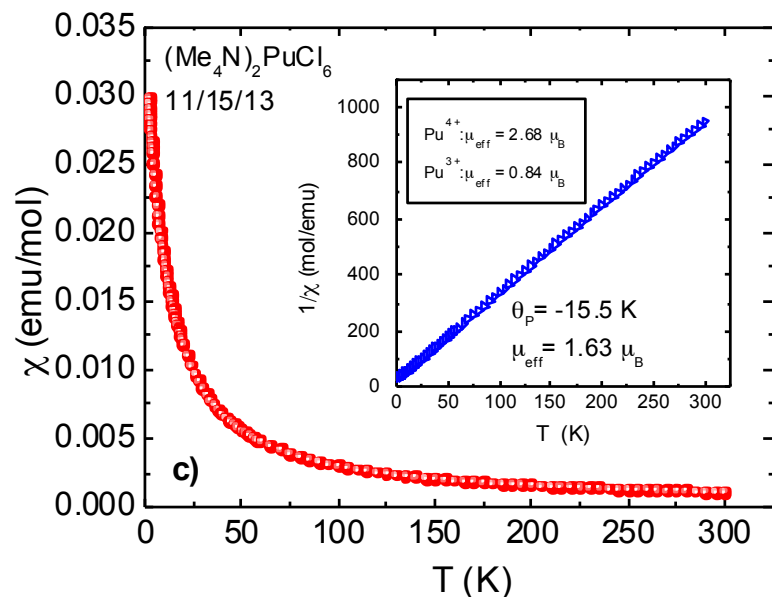


Search for ^{239}Pu NMR in $(\text{Me}_4\text{N})_2\text{PuCl}_6$

- Magnetic susceptibility indicates magnetic triplet ground state, rather than singlet ground state
- Calculations and modeling confirm this assessment



A. Mounce *et al.* Inorg Chem, 2016, in press



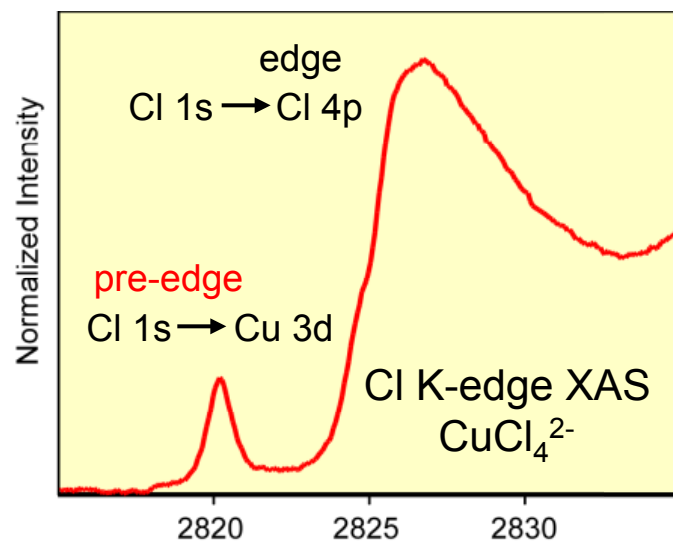
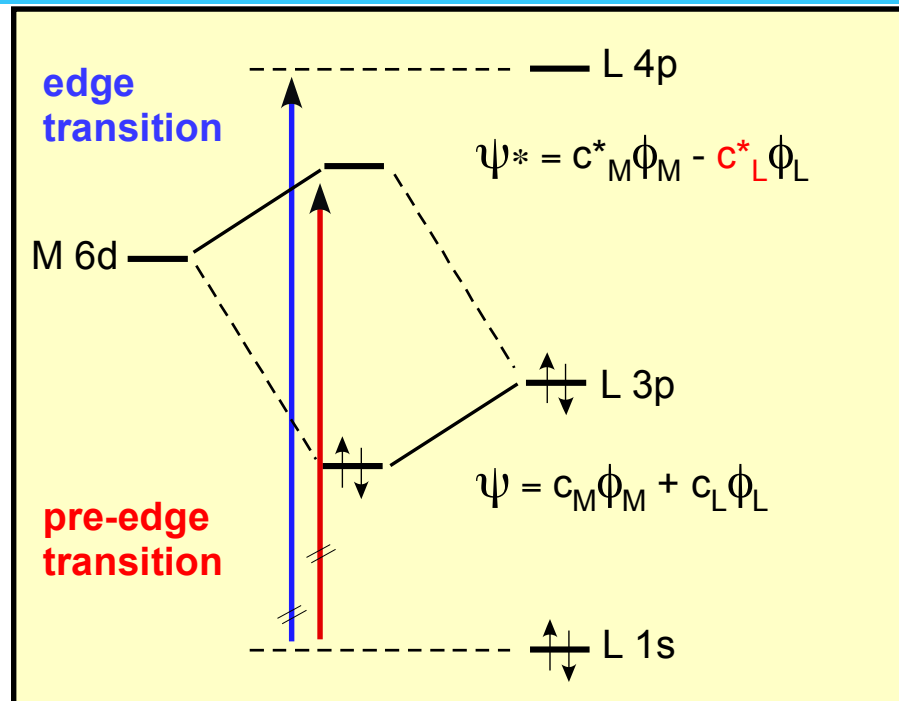
Covalent Mixing: Ligand K-edge XAS

- If metal forms covalent bonds with L 3p orbitals, then ψ^* has L 3p character

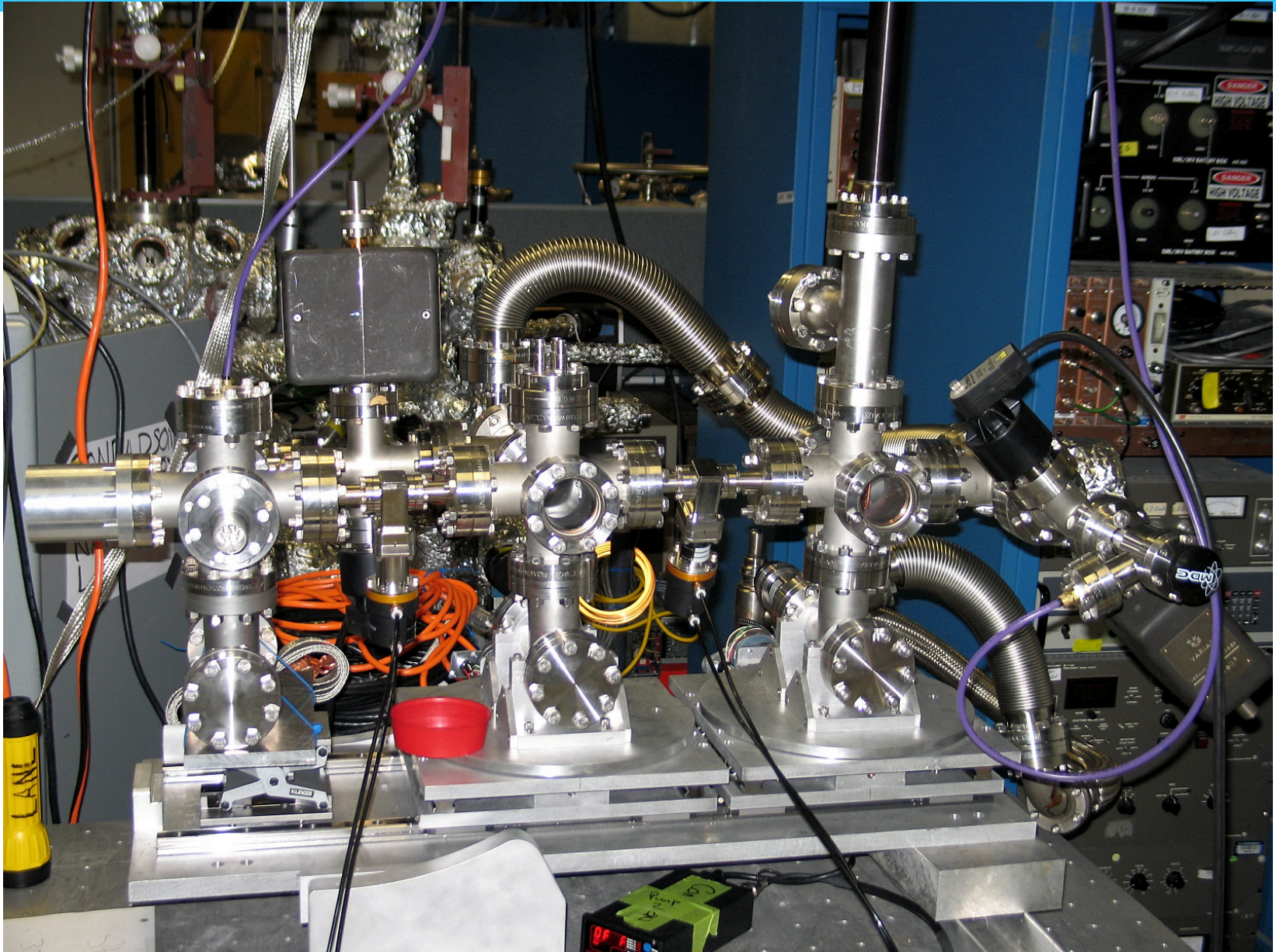
$$\psi^* = c_M^* \phi_M - c_L^* \phi_L$$

- Pre-edge transition may be described as L 1s \rightarrow ψ^* , where intensity is gained from L 3p character in ψ^*
- Pre-edge transition intensity derived from L-centered 1s \rightarrow 3p transition, weighted by c_L^{*2} , the covalent character of L 3p orbitals in ψ^*

Ligand K-edge XAS is a direct, quantitative probe of covalency in M-L bond

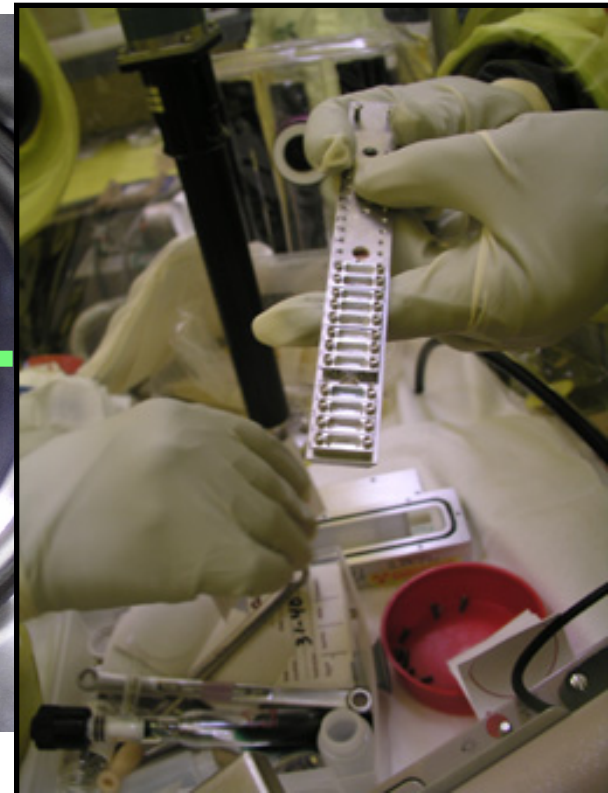
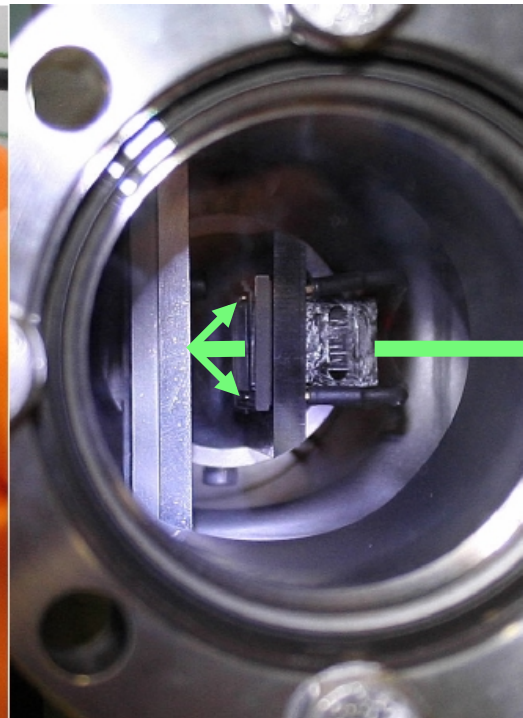
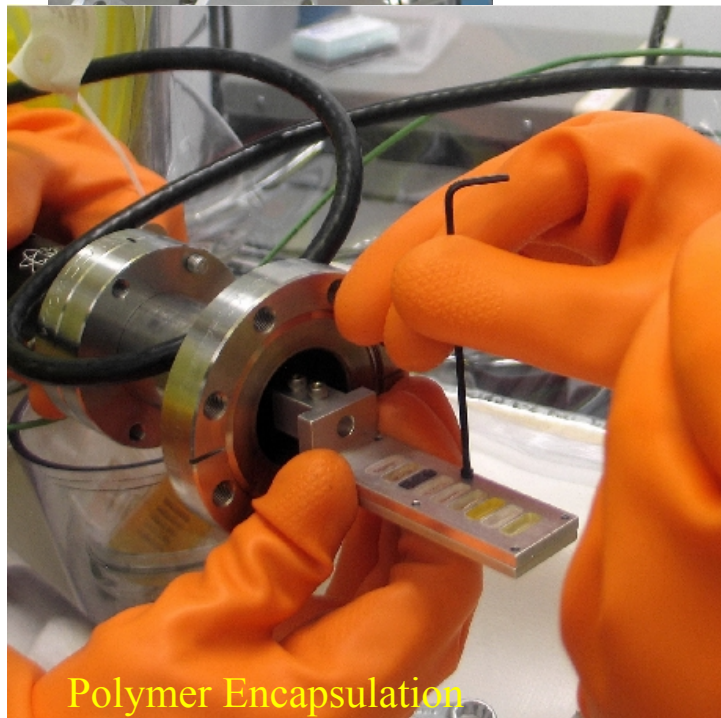
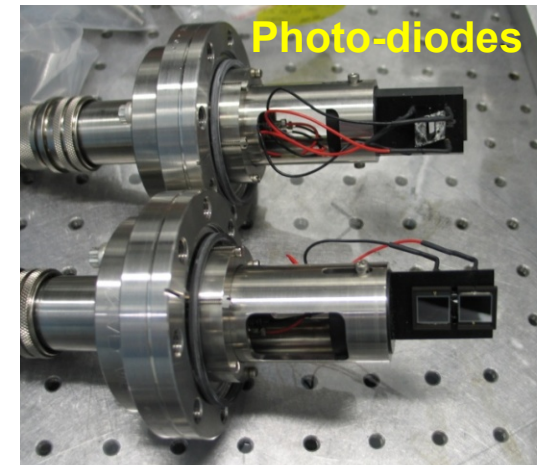


UHV Experimental Setup: 200 – 5000 keV

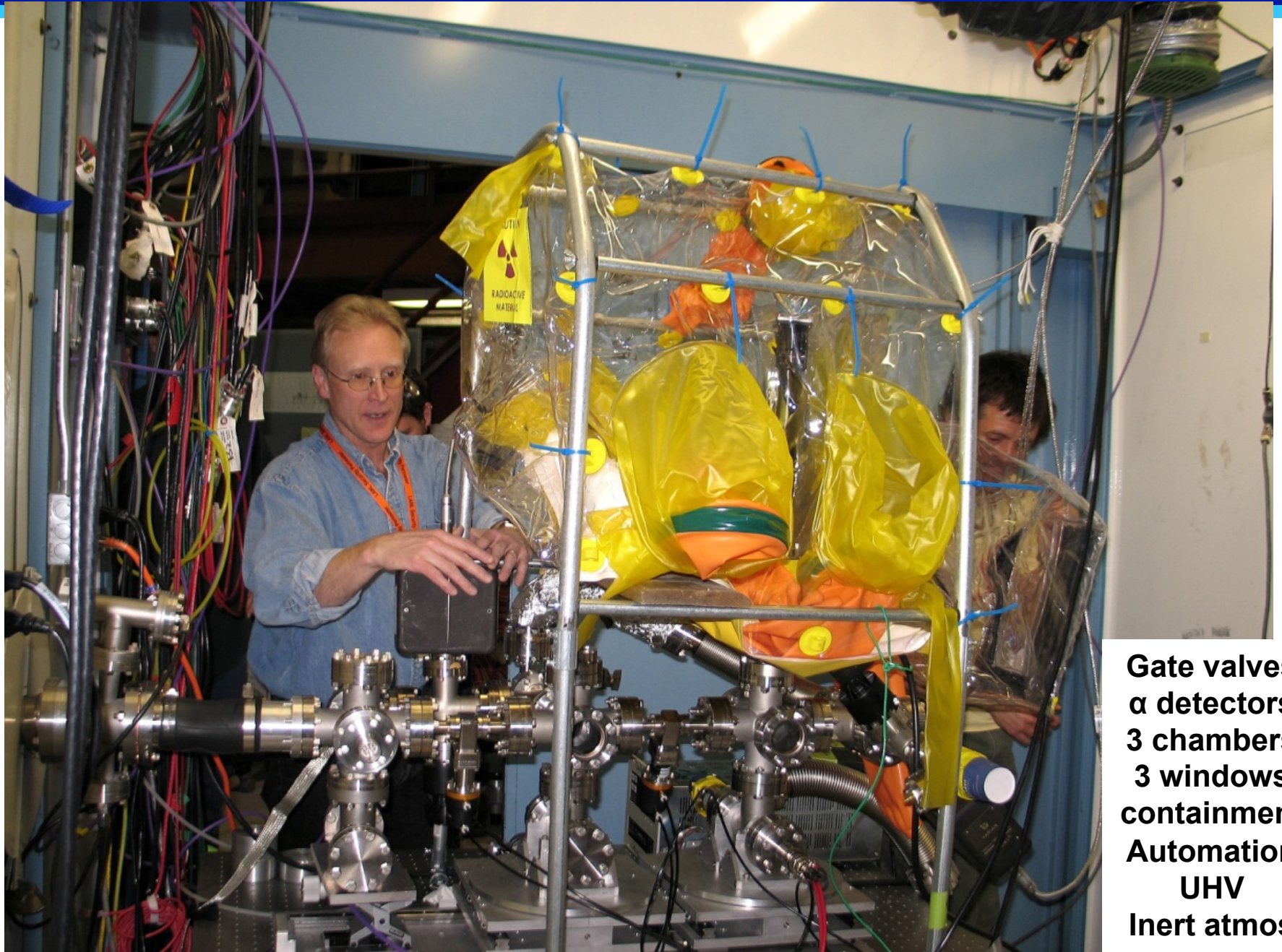


“how’ s the plumbing?”

Air Sensitive, Radioactive, Soft X-ray UHV Setup



Air-sensitive Radioactive K-edge XAS



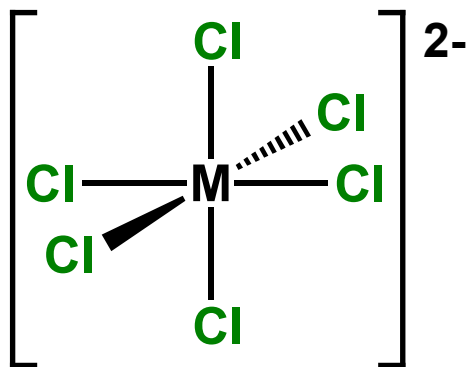
**Gate valves
 α detectors
3 chambers
3 windows
containment
Automation
UHV
Inert atmos**

The Nike step – do whatever it takes

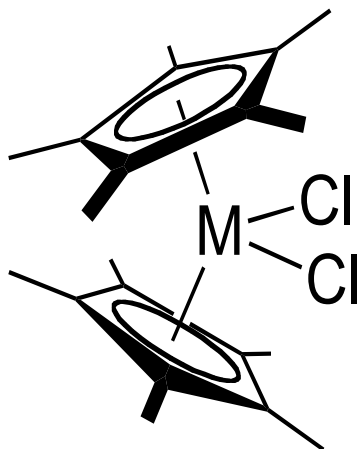


Benchmark molecules for Ligand K-edge XAS

Chlorine K-edge XAS

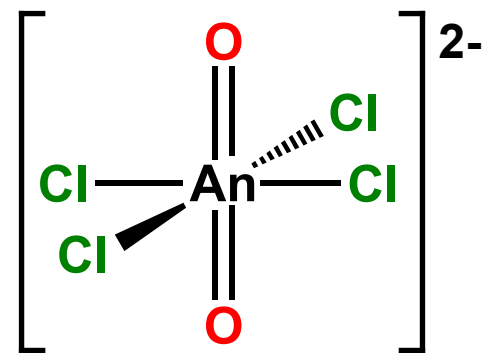


M = Ti, Zr, Hf, Th, U, Np, Pu

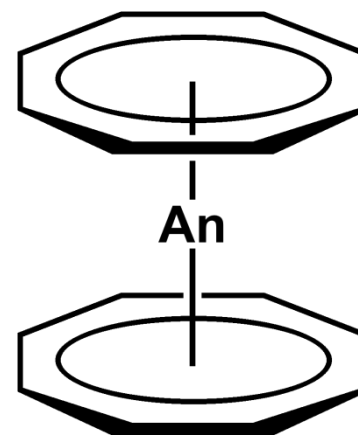


M = Ti, Zr, Hf, Th, U

C or O K-edge XAS



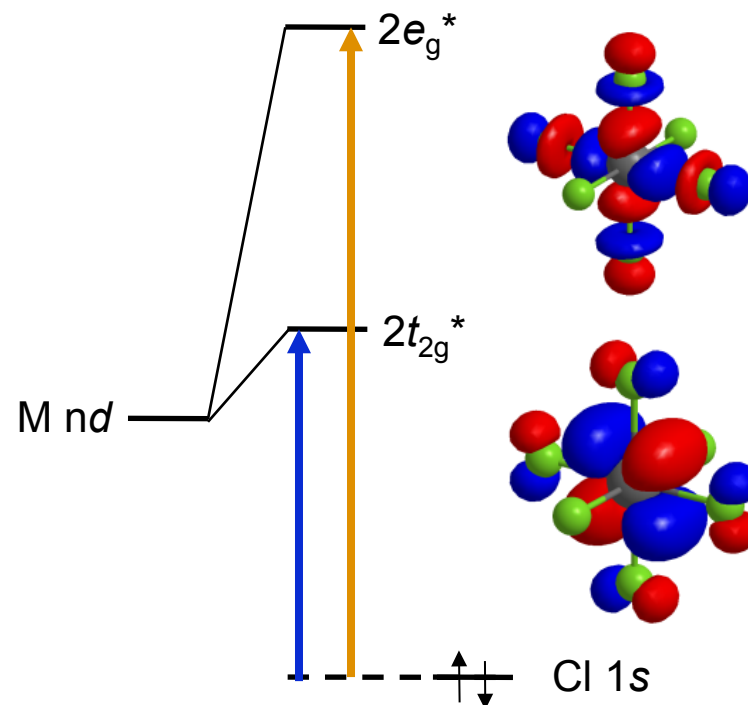
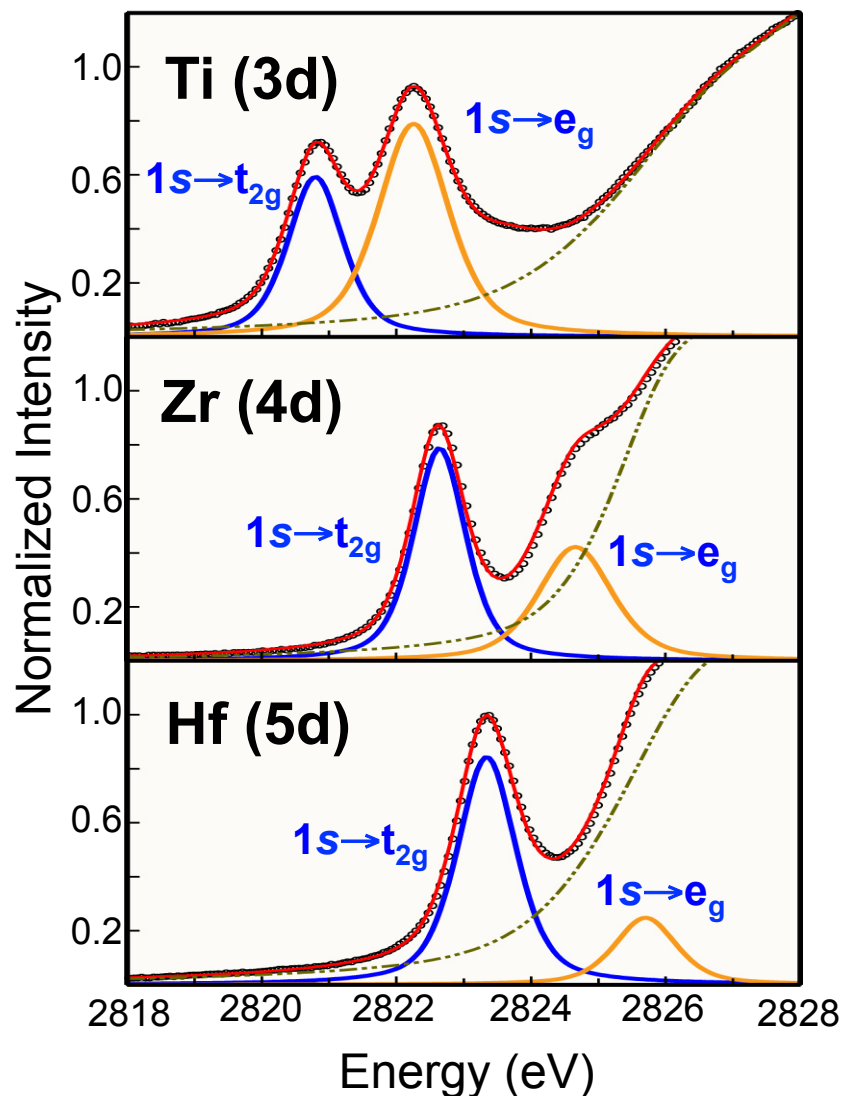
An = U, Np, Pu



An = Th, U, Np, Pu

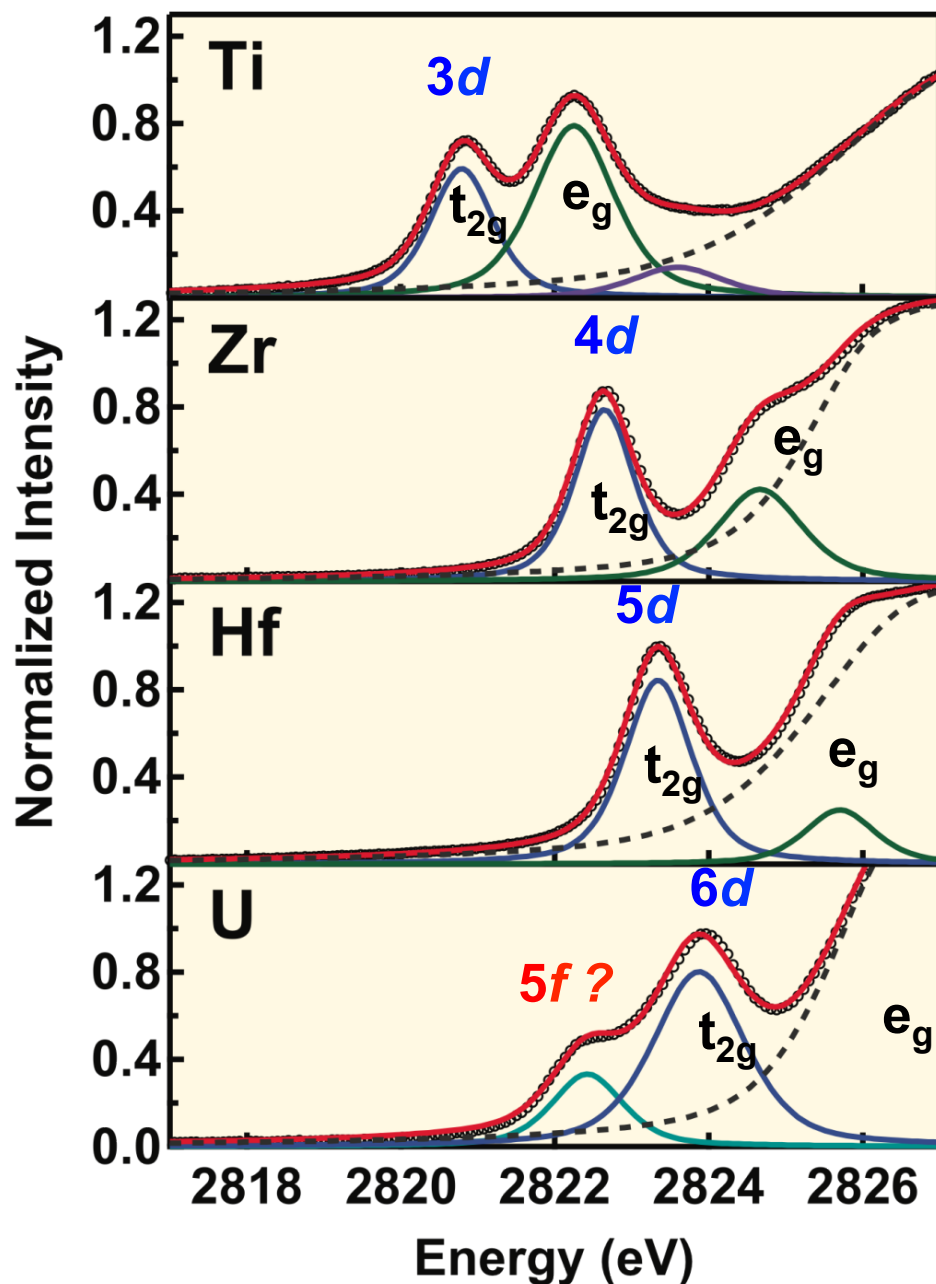
Cl K-edge XAS for octahedral Group IV MCl_6^{2-}

Increased Z results in increased pre-edge peak energy, splitting, and intensity.



% Cl 3p in t_{2g}	
Ti-Cl	8(1)
Zr-Cl	11(1)
Hf-Cl	13(1)

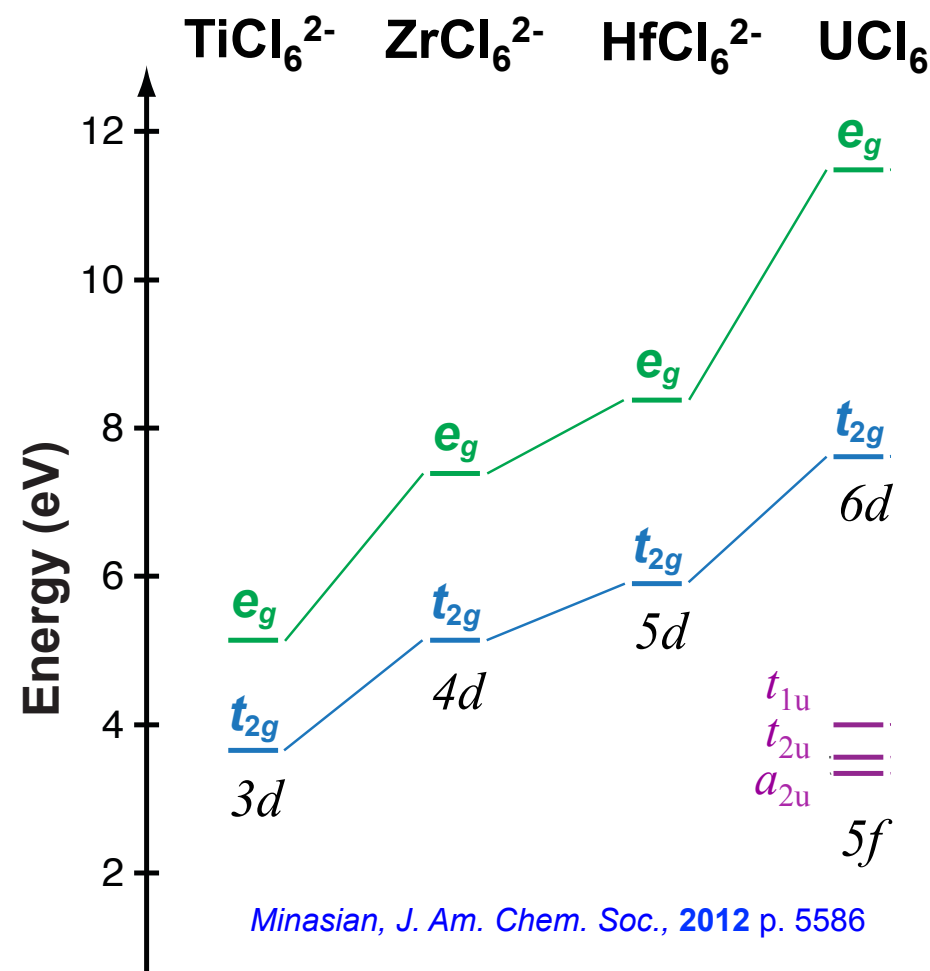
Cl K-edge XAS for octahedral Group MCl_6^{2-}



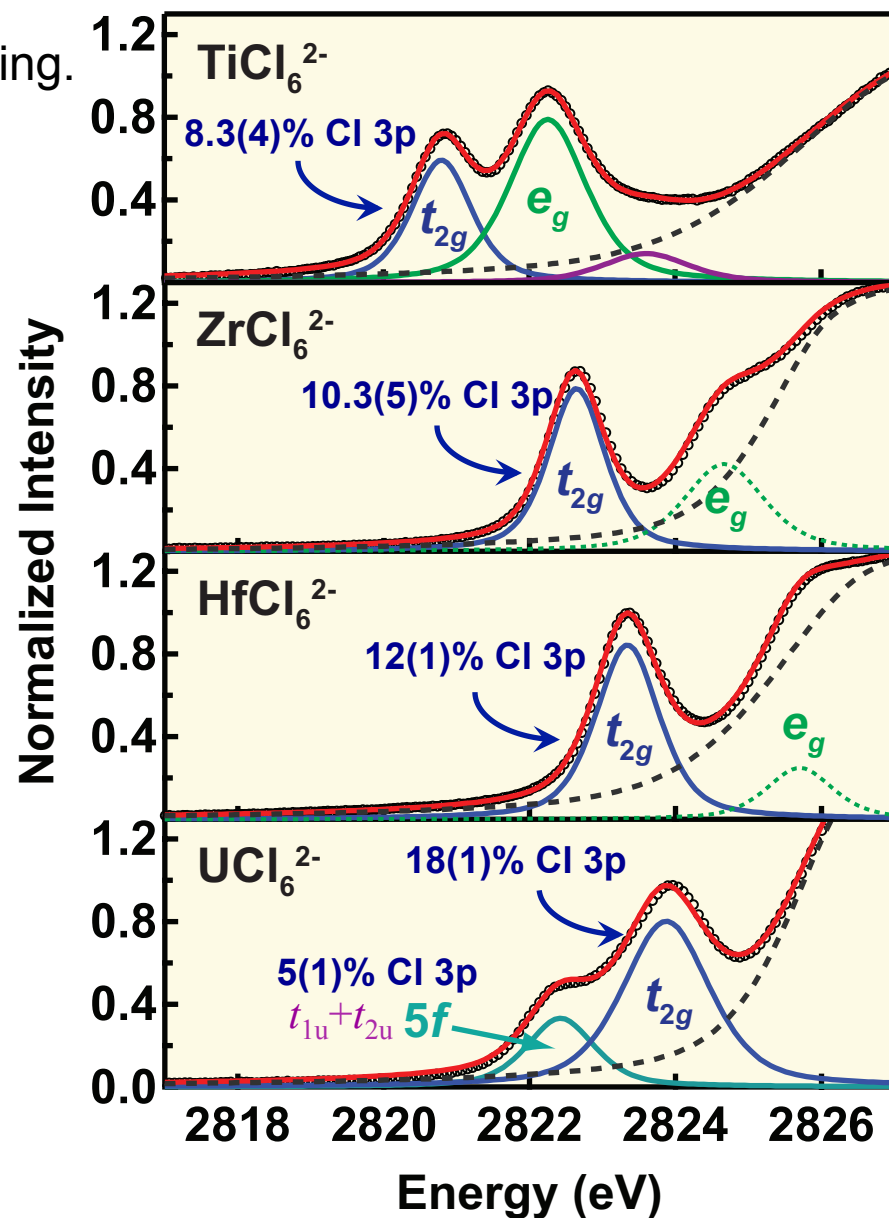
- **Pre-edge features confirm covalent mixing in MCl_6^{2-}**
- Transitions into d orbitals move to higher energy with increasing Z_{eff}
- Transitions to e_g move under white line with increasing Z_{eff}
- New peak in UCl_6^{2-} could be evidence for 5f mixing with Cl 3p

XAS & Electronic Structure Theory for MCl_6^{2-}

- Experiments at the Cl K-edge demonstrate both 5f- and 6d-orbital involvement in bonding.
- Trends in bonding can vary significantly depending on ligand, geometry, oxidation state.

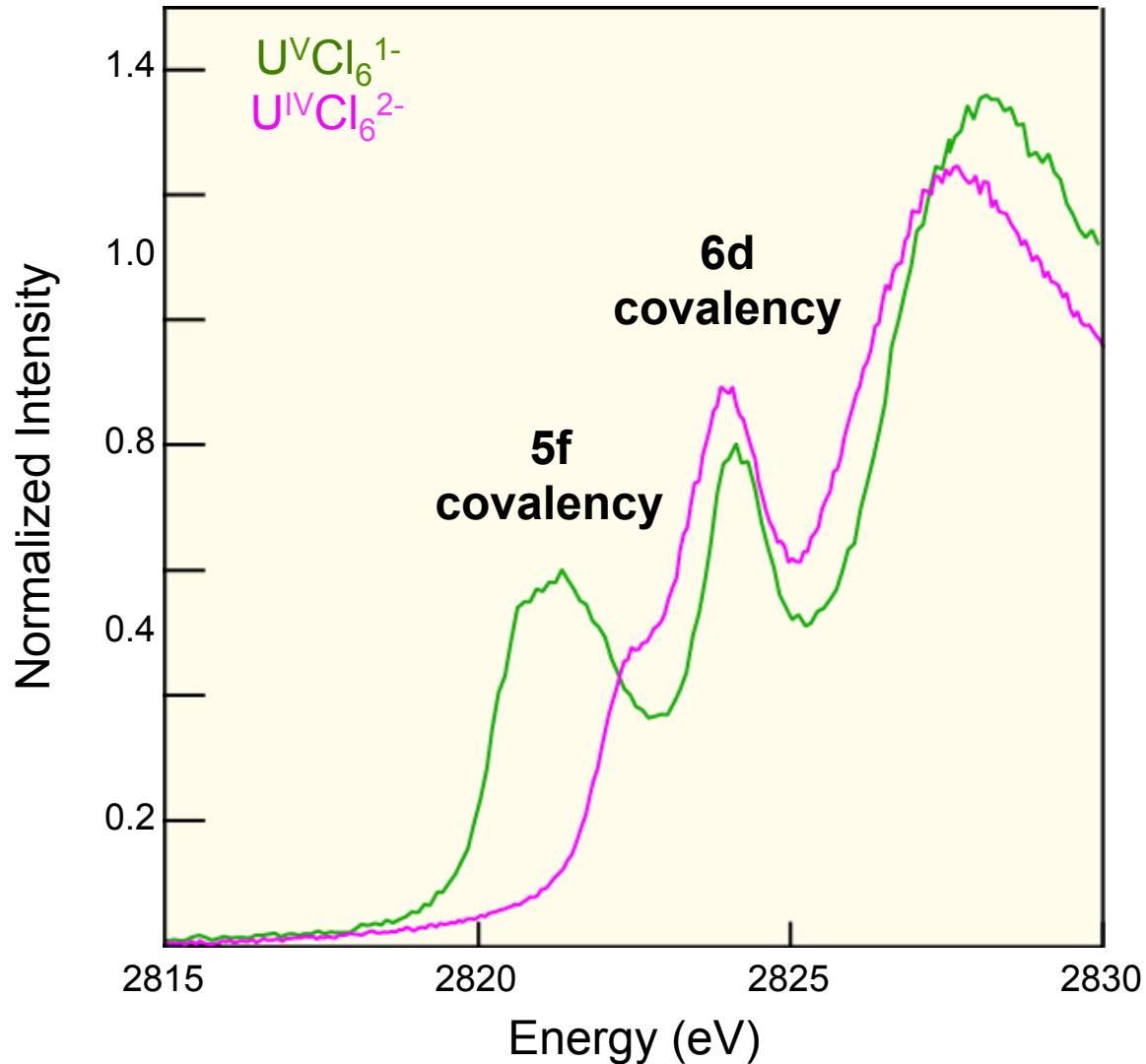


Minasian, J. Am. Chem. Soc., 2012 p. 5586



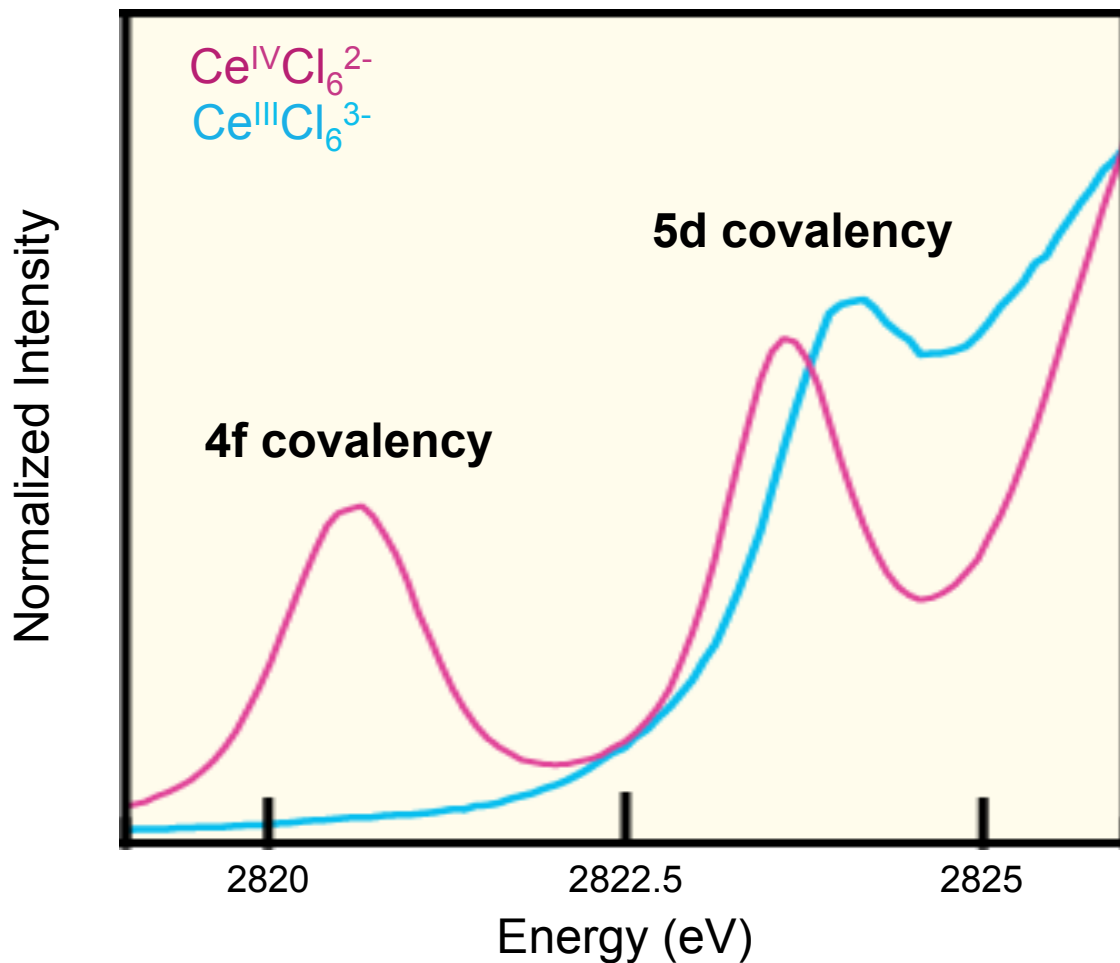
The Cl K-Edge XAS Spectra of UCl_6^{x-} ($x = 1, 2$)

The U 5f and Cl 3p mixing in UCl_6^{1-} is more pronounced than in UCl_6^{2-} .

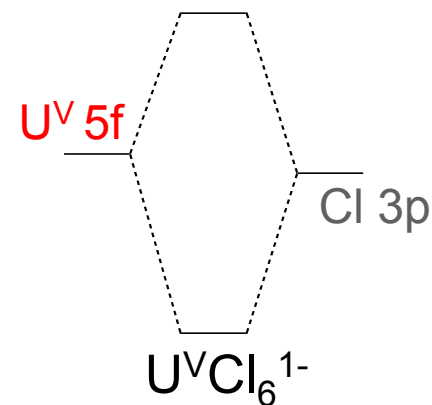
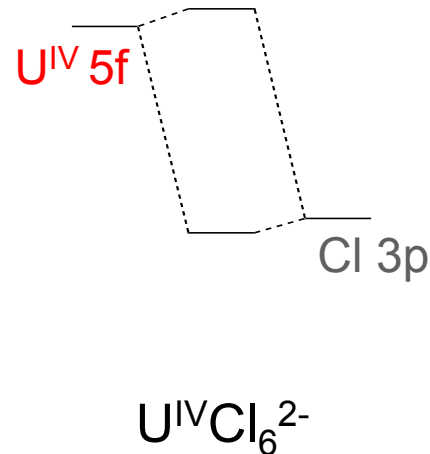
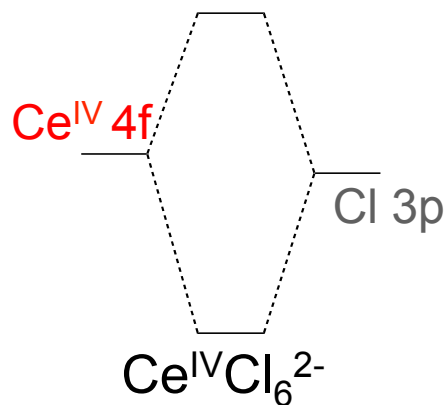
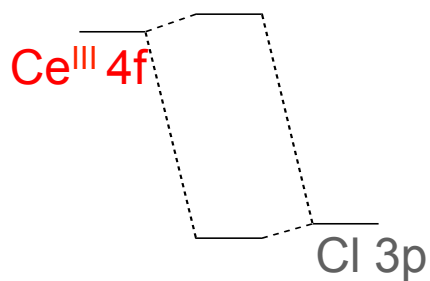
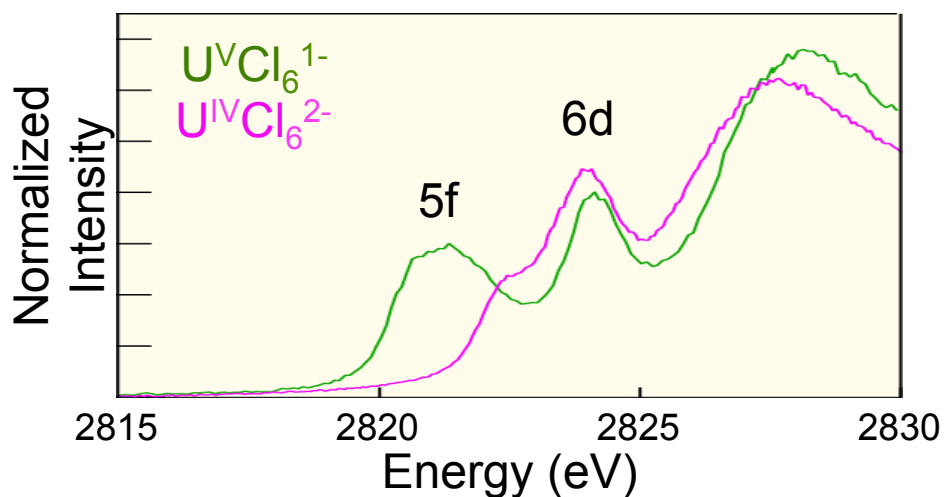
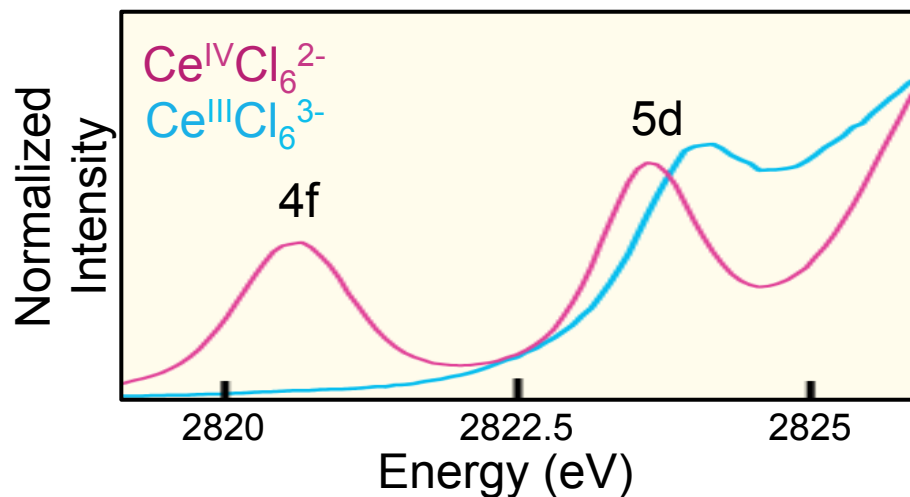


The Cl K-edge XAS Spectra of CeCl_6^{2-} vs CeCl_6^{3-}

The Cl K-edge XAS shows the 4f contribution to covalent Ce–Cl bonding is surprisingly more pronounced than the trivalent lanthanides.



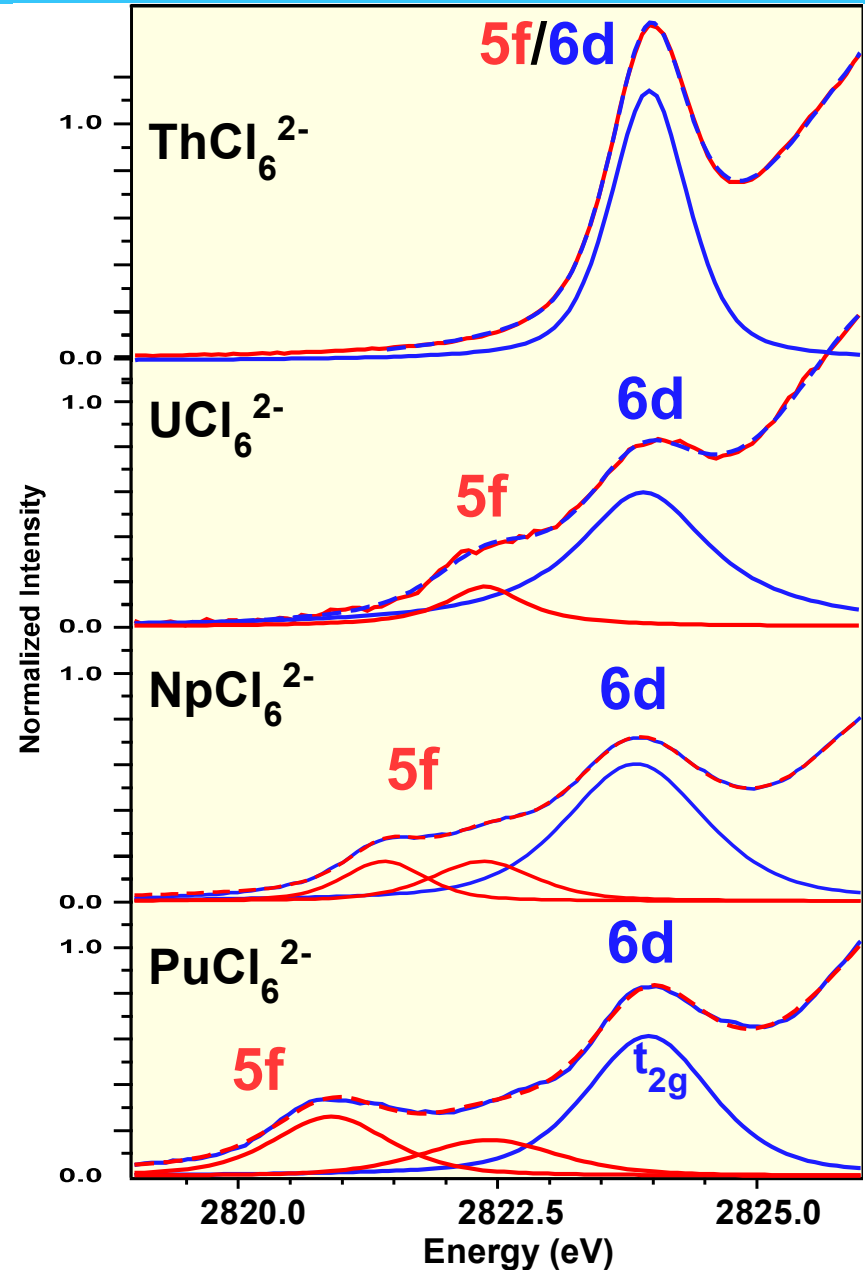
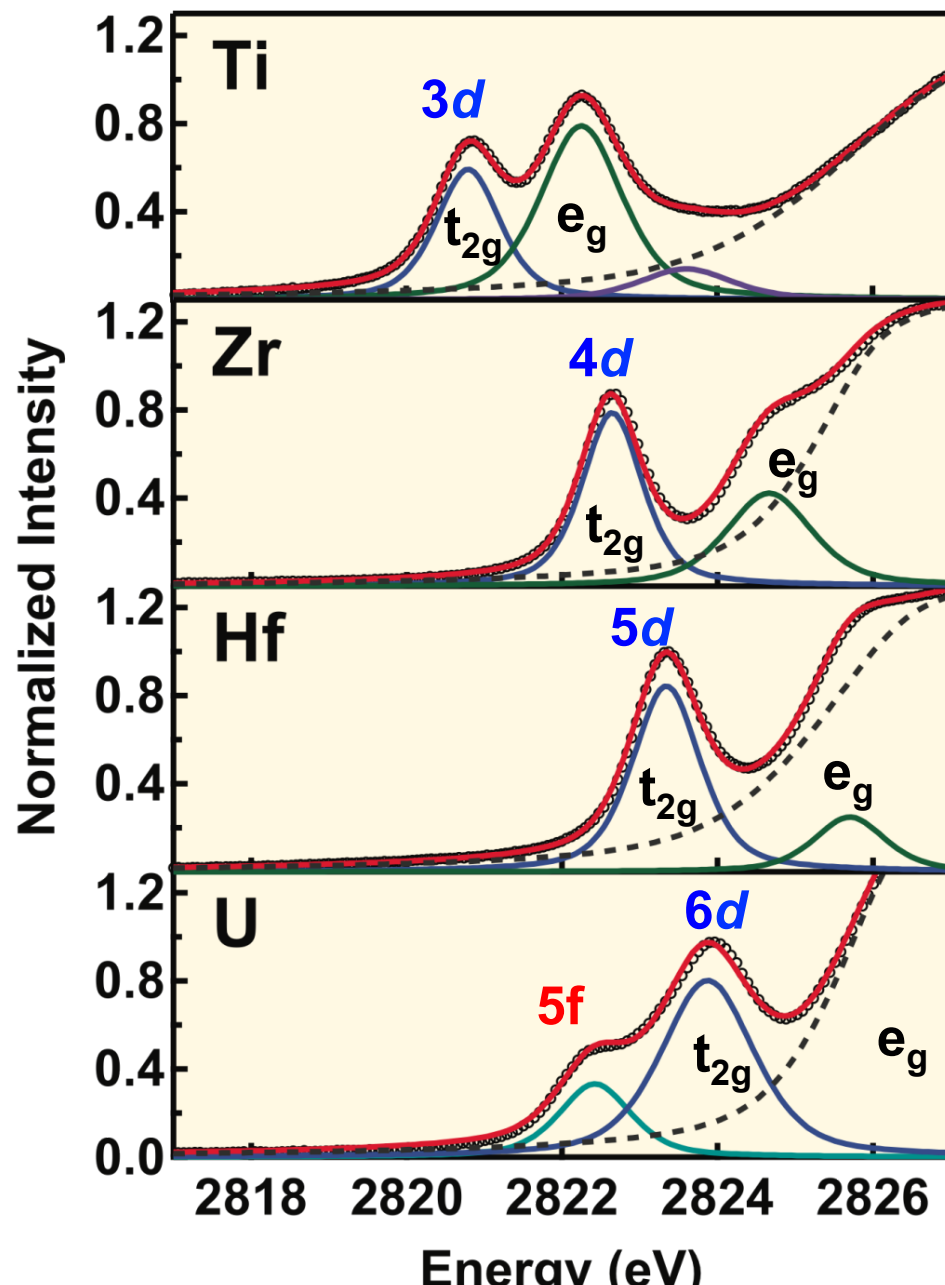
The Influence of Oxidation State



Increases in oxidation state provides better increases *f*-orbital mixing.

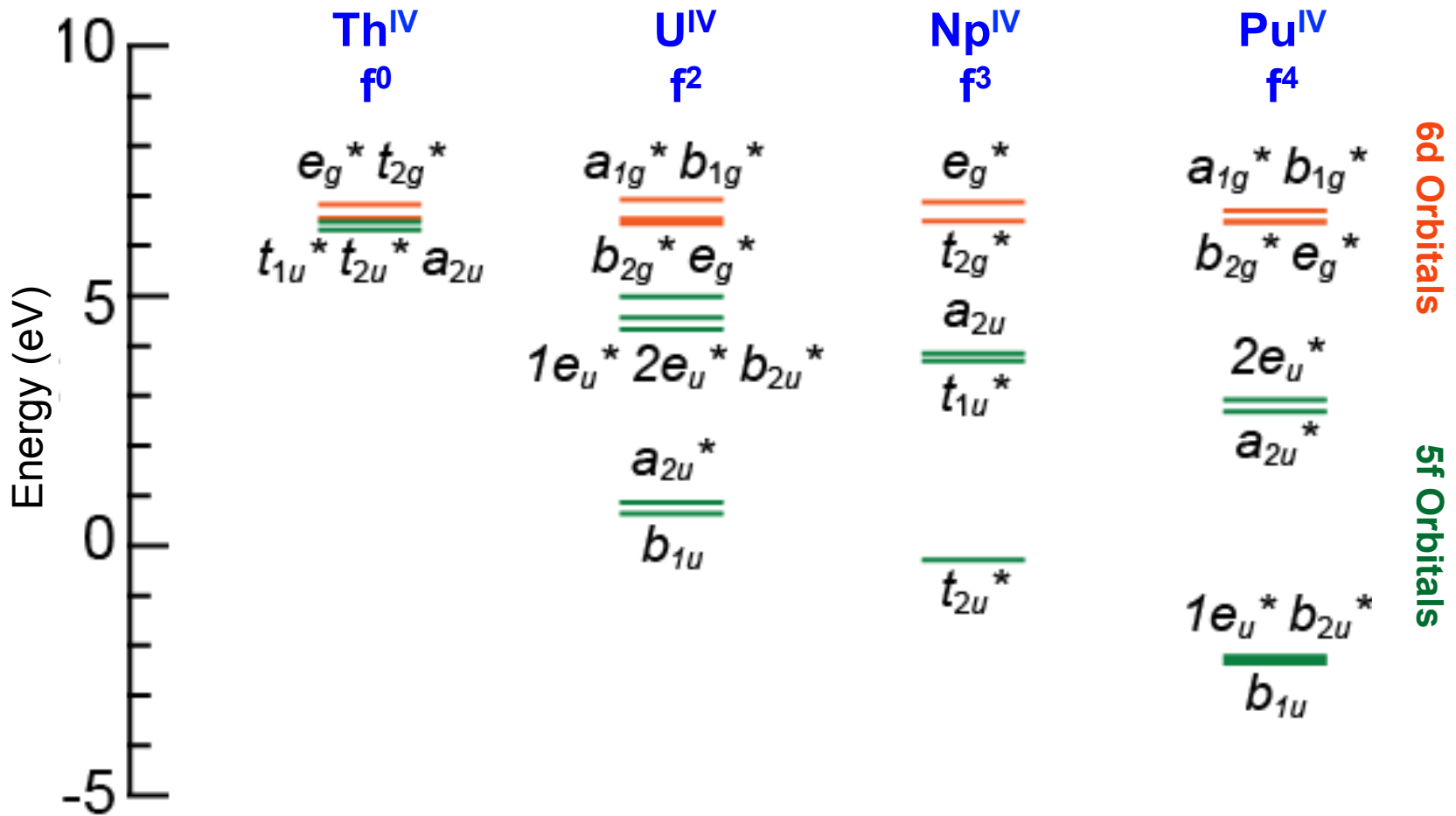
$$\lambda \approx \frac{-S_{\text{Metal-Ligand}}}{e_{\text{Metal}}^0 - e_{\text{Ligand}}^0}$$

Cl K-edge XAS Studies for MCl_6^{2-} systems



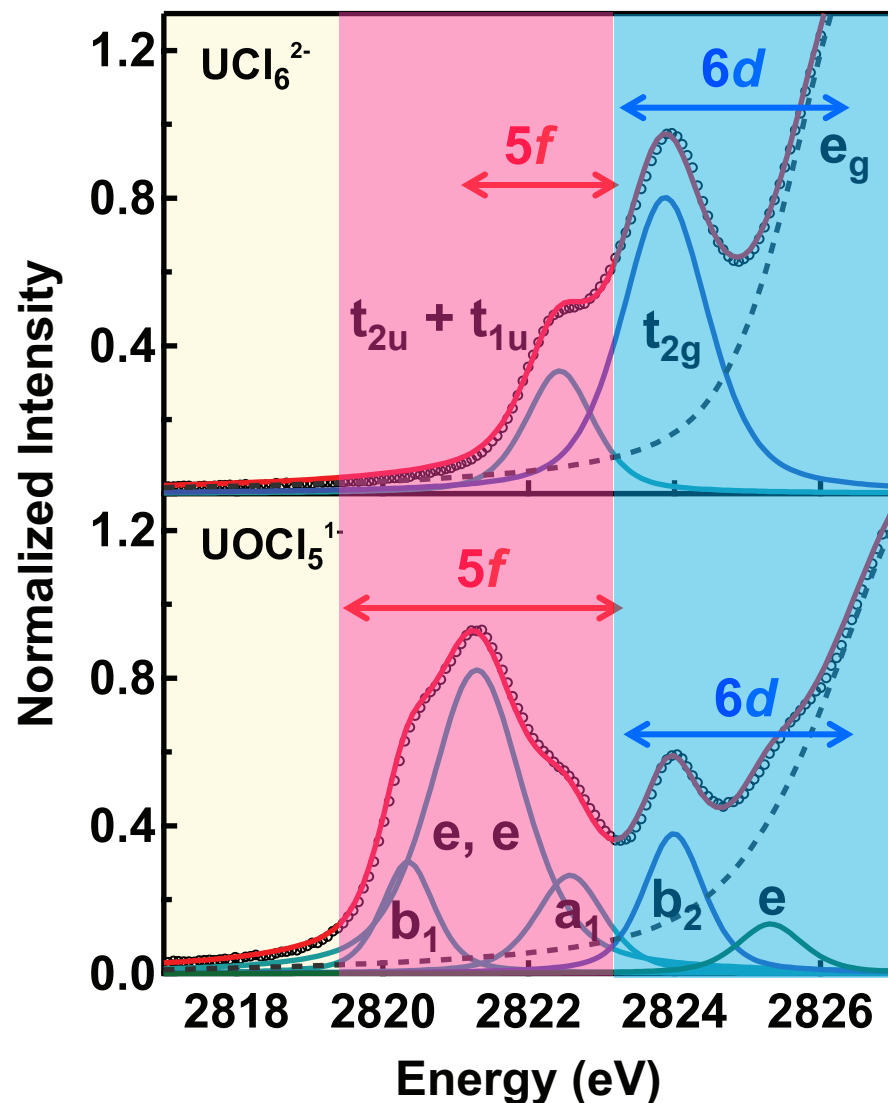
Molecular Orbital Interactions For AnCl_6^{2-}

Across the actinide series, the energy for the 6d-orbitals was relatively constant while that for the 5f-orbitals decreased.



What can we say about covalency?

- O_h MCl_6^{n-} complexes of **Ti, Zr, Hf, Th, U, Np, Pu**, demonstrate **evidence for covalent mixing**
- Pre-edge XAS features can be grouped into **5f** and **6d** regions of spectra
- For An ions, **6d** orbitals play dominant role, **5f** orbitals show “unexpected increase in mixing with Z_{eff} ”
- Covalency changes with M oxidation state, with Z_{eff} , and L orbital energetics (Cl vs S)
- Multiplet effects are becoming important for heavy elements with large numbers of unpaired electrons f^3 , f^4 (Np(IV), Pu(IV))



Acknowledgements

Enrique R. Batista
Eric D. Bauer
Kevin S. Boland
Scott R. Daly
Steven D. Conradson
Jason M. Keith
Stosh A. Kozimor
Georgios Koutroulakis
Juan Lezama

Mathias Loble
Richard L. Martin
John Matonic
Stefan Minasian
Andrew Mounce
Gregory L. Wagner
Marianne P. Wilkerson
Ping Yang
Hiroshi Yasuoka

LANL Seaborg Institute
& *LBNL Seaborg Center*
Postdoctoral Fellowships



Los Alamos National Laboratory

